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Contribution from the Sheffield Laboratory of Yale University.

ON HALOGEN ADDITION-PRODUCTS OF THE ANILIDES.

[SECOND PAPER.]

BY H. L. WHEELER AND P. T. WALDEN.

A preliminary notice was recently given by one of us (Wheeler) on halogen addition-products of the anilides.[1] In the case of metanitroacetanilide[1] products were prepared which contained bromine in various proportions, but, under certain conditions, the total bromine approximated to that calculated for a dibromine addition-product. These products have now been thoroughly reinvestigated and it has been found that, besides free bromine, they contain hydrobromic acid, and that the products described as dibromine addition-products of metanitroacetanilide were mixtures of the perhalides $(C_6H_4.NO_2.NHCOCH_3)_2HBr.Br_2$ and $[C_6H_4.NO_2.NHCOCH_3]_2HBr.Br_4$.

We have attempted to prepare bromine addition-products of metanitroacetanilide and parabromacetanilide, in the absence of hydrobromic acid, but without success. Bromine free from hydrobromic acid can be mixed with these anilides,

[1] This JOURNAL, 17, 612.

when suspended in pure carbon bisulphide, without any addition taking place. The unaltered anilides are recovered on filtering and drying. When, on the other hand, bromine containing hydrobromic acid or solvents which are attacked by bromine—such as chloroform, glacial acetic acid, or ligroïn—are used, perhalides are formed.

It has been found in general that when bromine is mixed with an anilide under conditions which permit of the formation of hydrobromic acid, the hydrobromic acid unites with the anilide to form an ammonium salt, *i.e.* $[R.NHCOCH_3]_3HBr$[1] and that this salt then adds bromine.

We have prepared the salts $[C_6H_4.NO_2.NHCOCH_3]_3HBr$ from metanitroacetanilide; $[C_6H_4.Br.NHCOCH_3]_3HBr$ from parabromacetanilide; and $[C_6H_5.NHCOCH_3]_3HI$ from acetanilide. These salts gave the following series of halogen addition-products:

$[C_6H_4.NO_2.NHCOCH_3]_3HBr.Br_2$.
$[C_6H_4.NO_2.NHCOCH_3]_3HBr.Br_4$.
$[C_6H_4.NO_2.NHCOCH_3]_3HBr.Br_6$.
$[C_6H_4.Br.NHCOCH_3]_3HBr.Br_2$.
$[C_6H_4.Br.NHCOCH_3]_3HBr.Br_4$.
$[C_6H_5.NHCOCH_3]_3HI.I_2$.
$[C_6H_5.NHCOCH_3]_3HI.I_4$.

These compounds are perfectly analogous to the perhalides $CsBr.Br_2$[2], $CsI.I_2$[3], and $NH_4Br.Br_2$[4]. No perhalides of the salts of the anilides have hitherto been described, but perhalides of other organic halides have frequently been observed, of which the following are examples: $C_6H_5N.N—Br.Br_2$;[5] $[C_5H_7N]_3HBr.Br_4$[6]; $C_6H_5(CH_3)_3NI.I_2$; $C_6H_5(CH_3)_3NI.I_4$; and $C_6H_5.C_5H_5(CH_3)_2NI.I_6$.[7]

Method of Analysis.—In order to determine total bromine the weighed sample was treated with dilute ammonia, and in no case were the products analyzed which did not give the un-

[1] Compare Nölting and Weingärtner: Ber. d. chem. Ges., **18**, 1340; also Roozeboom: Chem. Centrbl, **1886**, 498.
[2] Wells: Am. J. Sci., **43**, 27.
[3] Wells and Wheeler: *Ibid*, **44**, 43.
[4] Roozeboom: Ber. d. chem. Ges., **14**, 2398.
[5] Hantzsch: Ber. d. chem. Ges., **28**, 2754.
[6] Grimaux: Bull. Soc. Chim. (Paris), **38**, 127.
[7] Geyther: Ann. Chem. (Liebig), **240**, 66.

altered anilide with a correct melting-point. The solutions were then acidified with nitric acid and the bromine determined by means of Volhard's[1] volumetric method. In another sample free bromine was determined by weighing the substance into a solution of potassium iodide and then titrating the liberated iodine with a tenth-normal sodium thiosulphate solution. From the difference the hydrobromic acid was calculated. Total iodine was also determined by Volhard's method, the free iodine having been converted into hydriodic acid by means of a solution of sodium arsenate in sodium bicarbonate. Free iodine was determined in a separate sample by means of the sodium thiosulphate solution, and the hydrogen iodide by difference.

Experiments with Metanitroacetanilide.

The 1 : 1 *hydrobromide*, $C_6H_4.NO_2.NHCOCH_3.HBr$, was obtained as a colorless crystalline precipitate when hydrobromic acid gas was led into a chloroform solution of the anilide. It was dried on paper in the air.

	Found.		Calculated for $C_8H_8N_2O_3.HBr$.
	I.	II.	
HBr	30.5	30.8	30.9

The 2 : 1 *hydrobromide*, $[C_6H_4.NO_2.NHCOCH_3]_2.HBr$.— This and the preceding salt were described in the preliminary paper.[2] It seems to be formed when the 1 : 1 salt is treated with glacial acetic acid since perhalides of this salt were invariably obtained when bromine was added to the 1 : 1 salt in the presence of glacial acetic acid.

The *trihalide*, $[C_6H_4.NO_2.NHCOCH_3]_2.HBr.Br_2$. — 2.5 grams of the 1 : 1 hydrobromide were covered with 25 grams of glacial acetic acid (containing some hydrobromic acid) and 3 grams of bromine added. On warming gently, filtering and cooling, beautiful light orange-colored flattened prisms separated. These were washed with chloroform and dried by pressing on filter-paper.

	Found.	Calculated for $C_{14}H_{14}N_4O_6.HBr.Br_2$.
Br (total)	39.2	39.9
Br (free)	26.2	26.6
HBr	13.1	13.4

[1] Ann. Chem. (Liebig), **190**, 1. [2] *Loc. cit.*

The *pentahalide*, $[C_6H_4.NO_2.NHCOCH_3]_2.HBr.Br_4$, was prepared by suspending the 1 : 1 hydrobromic-acid salt in chloroform and adding bromine in the proportion of 1 molecule of the salt to about 12 atoms of bromine. Solution was effected by warming and adding small quantities of glacial acetic acid. On filtering and cooling, deep orange-colored prisms separated [Analysis I]. This compound was also obtained when 3.5 grams of the 1 : 1 salt were mixed with 11 grams of bromine in 13.8 grams of glacial acetic acid containing a little hydrobromic acid gas [Analysis II].

The crystals that separated from the solution were washed with chloroform containing a little bromine. The material for analysis was dried on paper as rapidly as possible.

	Found. I.	Found. II.	Calculated for $C_{16}H_{14}N_4O_6.HBr.Br_4$.
Br (total)	52.7	51.2	52.5
Br (free)	42.6	40.4	42.0
HBr	10.2	10.8	10.6

The *heptahalide*, $(C_6H_4.NO_2.NHCOCH_3)_2.HBr.Br_6$, was obtained by suspending 3.5 grams of the 1 : 1 hydrobromic-acid salt in 7.8 grams of cold glacial acetic acid (containing hydrobromic acid); to this 58.8 grams of bromine were then added and the whole warmed to a blood heat. On cooling to —10° long brick-red needles separated. These were washed free from glacial acetic acid by means of bromine which had been cooled to —10°. The material was drained on the pump, then on a porous plate, and finally pressed on paper [Analysis I]. A portion was exposed somewhat longer than I. to the air [Analysis II].

	Found. I.	Found. II	Calculated for $C_{16}H_{14}N_4O_6.HBr.Br_6$.
Br (total)	61.0	61.3	60.8
Br (free)	53.5	53.0	52.1
HBr	7.5	8.4	8.8

Experiments with Parabromacetanilide.

The 2 : 1 *hydrobromide*, $(C_6H_4.Br.NHCOCH_3)_2.HBr$. — This and not the 1 : 1 salt was obtained when a chloroform solution of the anilide was treated with hydrobromic acid gas. It consisted of colorless needles.

	Found. I.	Found. II.	Calculated for $C_{16}H_{16}N_2O_2Br_2.HBr$.
HBr	15.4	15.9	15.9

The *trihalide*, $(C_6H_4.Br.NHCOCH_3)_2.HBr.Br_2$, was obtained by adding ligroïn to a solution of the above hydrobromic-acid salt in a mixture of ethyl acetate, chloroform, and bromine. The precipitate thus produced was crystallized from chloroform containing some glacial acetic acid. Beautiful, flattened, light-orange colored prisms separated.

	Found.	Calculated for $C_{16}H_{14}N_2O_2Br_2.HBr.Br_2$.
Br (total)	35.8	35.9
Br (free)	24.9	23.9
HBr	10.9	12.1

The *pentahalide*, $(C_6H_4.Br.NHCOCH_3)_2HBr.Br_4$, was obtained by suspending the salt in chloroform, adding a large excess of bromine, and then warming with the addition of small quantities of glacial acetic acid until the whole dissolved. On cooling, small flattened crystals separated. These had a deep orange color.

	Found.		Calculated for $C_{16}H_{14}N_2O_2Br_2.HBr.Br_4$.
	I.	II.	
Br (total)	46.2	47.5	48.2
Br (free)	36.3	36.3	38.6
HBr	9.8	11.3	9.7

Experiments with Acetanilide.

The 2:1 *hydroiodide*, $(C_6H_5.NHCOCH_3)_2.HI$, separated from a solution of acetanilide in ethyl acetate in the form of shining colorless scales, when hydrogen iodide was led into the solution.

	Found.	Calculated for $C_{16}H_{16}N_2O_2.HI$.
HI	32.2	32.1

The *trihalide*, $(C_6H_5.NHCOCH_3)_2.HI.I_2$.—A solution of 4.1 grams of the above salt, with 2.6 grams iodine in 15 grams of glacial acetic acid deposited ruby-red crystals. These were analyzed with the following result:

	Found.	Calculated for $C_{16}H_{18}N_2O_2.HI.I_2$.
I (total)	58.0	58.4
I (free)	39.0	38.9
HI	19.1	19.6

The *pentahalide*, $(C_6H_5.NHCOCH_3)_2.HI.I_4$, was obtained from a glacial acetic-acid solution of the constituents. It

forms glistening prisms of a deep reddish-brown color with the lustre of iodine. They transmit a deep red-brown light.

	Found.	Calculated for $C_{18}H_{18}N_2O_2.HI.I_4$.
I (total)	70.1	70.0
I (free)	57.4	56.0
HI	12.8	14.1

THE ACTION OF THE HALOGENS ON THE METHYLAMINES.

By Ira Remsen and James F. Norris.

In the course of an investigation of the double halides of selenium and the aliphatic amines, the results of which will be published later, a salt of the composition represented by the formula $SeBr_4.SeOBr_2.2(CH_3)_3N.HBr$, was brought to light. This was treated with bromine in order, if possible, to convert it into the salt of the composition $SeBr_4.(CH_3)_3N.HBr$. A crystalline precipitate was obtained, which proved to be something quite different from what was expected. The product dissolved in water with evolution of bromine, and was found not to contain selenium. This led to experiments with trimethylamine and bromine, and afterward, to experiments with the other halogens and other substituted ammonias. At first trimethylamine hydrobromide was treated with bromine, and a compound obtained that contained one more atom of bromine than the hydrobromide. The formula $(CH_3)_3N.HBr.Br$, with which the analytical results are in close agreement, appears highly improbable, and it was suspected that the composition should be represented by the formula $(CH_3)_3N.Br_2$, its formation being due to the substitution of bromine for the hydrogen of the hydrobromide. If this view is correct, the same product should be formed by the direct addition of bromine to trimethylamine. This formation was found to take place, and further experiments showed that this kind of addition can be effected in other similar cases. The following is an account of the work as far as it has been carried. It will be continued in the immediate future.

Historical.—The action of the halogens on the aliphatic amines has frequently been the subject of investigations.

Wurtz,[1] the discoverer of these amines, worked in water solution, and obtained products which he supposed to be formed by substitution of halogen atoms for hydrogen. Thus methylamine gave a dichloro-substitution product, which he believed to have been the constitution CH_3NCl_2. Ethylamine gave a similar product. Raschig[2] obtained a compound of the formula $(CH_3)_2HN.Br_2.2H_2O$, by treating a water solution of dimethylamine with bromine. By working in alkaline solutions other experimenters have obtained products similar to those discovered by Wurtz. Thus Raschig[3] obtained the compounds CH_3NI_2 and $(CH_3)_2NI$. Later Berg[4] and Séliwanow[5] prepared other halogen derivatives of the substituted ammonias, all of them being similar to those prepared by Wurtz and, therefore, quite different from those discovered by us.

A compound of ammonia with iodine perfectly analogous to those obtained by us has been prepared by Seamon[6] by passing dry ammonia over powdered iodine. The product, which was a dark-colored liquid, was shown to have the composition NH_3I_2. This was also prepared by Guthrie[7] by treating ammonium nitrate with potassium hydroxide and iodine.

Action of Bromine on Trimethylamine.

Trimethylamine, liberated from the chloride by potassium hydroxide and dried by sodium hydroxide, was conducted into a Peligot tube containing bromine cooled with ice-water. As the gas was absorbed a yellow precipitate separated. This was dried on a porous plate, and the last traces of free bromine removed by allowing the salt to stand over potassium hydroxide in a desiccator. It proved to be identical with the product formed by the action of bromine on trimethylamine hydrobromide. The latter method is the more convenient. To trimethylamine hydrobromide just enough concentrated hydrobromic acid is added to dissolve it when heated. Bromine, in the proportion 1 molecule to 1 molecule of the salt,

[1] Ann. chim. phys. [3]. **30**, 454. [2] Ber. d. chem. Ges., **18**, 2249.
[3] Ann. Chem. (Liebig), **330**, 221.
[4] Comptes rendus, **90**, 862; and "Thèses présentées a la Faculté des Sciences de Paris pour obtenir le grade de Docteur ès Sciences physiques." Paris, 1894.
[5] Ber. d. chem. Ges., **28**, 3621. [6] Chem. News, **44**, 188.
[7] J. chem. Soc. (London), 1863, 239.

is then added and the solution heated. On cooling, the product crystallizes out in light yellow plates. These can be recrystallized from absolute alcohol when they appear in the form of stout prismatic needles. Water alone instantly decomposes the salt with the liberation of half of the bromine. It is insoluble in ether. Analysis of the precipitate first obtained gave the following results:

I. 0.2530 gram salt gave off 0.0921 gram Br when dissolved in water.

II. 0.2443 gram salt gave 0.1781 gram Br after reduction of the free bromine by sulphur dioxide.

	Calculated for $(CH_3)_4NBr_3$.	Found. I.	II.
1 Atom Br	36.53	36.40	....
Total Br	73.06	....	72.90

The salt prepared by treating trimethylamine hydrobromide with bromine was analyzed:

0.2289 gram salt gave 0.1665 gram Br.

Total Br	73.06	Found	72.72

Action of Iodine on Trimethylamine.

Trimethylamine was passed into a solution of iodine in absolute alcohol, and in a short time a yellow precipitate appeared. This was filtered off and washed with absolute alcohol, then dried in a desiccator and analyzed. The properties of the iodide are different from those of the bromide. While the latter is decomposed by simple contact with water, the former is almost insoluble. To effect solution the water must be heated, when decomposition takes place slowly with liberation of iodine. Further, cold alcohol readily dissolves the bromide. Heat is necessary in the case of the iodide, and this causes partial decomposition. In the analysis of the compound the weighed portion was heated in a pressure bottle on a water-bath until the salt was completely decomposed. The total iodine was determined in one sample by reducing the free iodine with sulphur dioxide. The liberated iodine in another was dissolved in potassium iodide and titrated with sodium thiosulphate. The results of the analyses are here given:

I. 0.2820 gram salt gave 0.2293 gram I.
II. 0.3138 " " " 0.1455 " free I.

	Calculated for $(CH_3)_3NI_2$.	Found. I.	Found. II.
Total I	81.09	81.31	....
One Atom I	40.54	....	46.36

From the last analysis it is evident that the decomposition with water is different from that which the bromide undergoes. The amount of iodine set free is considerably more than one atom. This points to the formation of free hydriodic acid, for it was found that dilute acids liberate all of the iodine from the compound. The normal action would be the giving off of one atom of the iodine, but if hydriodic acid is set free at the same time, it would act upon a part of the compound and liberate two atoms of iodine for each molecule of the acid. The iodide when first prepared is of a light yellow color. It gradually darkens and changes to a dark brown viscous liquid. A portion of the salt was treated with dilute hydrochloric acid. There was immediate decomposition with liberation of iodine. This was titrated with sodium thiosulphate with the following result:

0.5319 gram salt gave 0.4287 gram I.

Iodine found 80.60. Theory 81.09.

Action of Chlorine on Trimethylamine.

Dry trimethylamine and dry chlorine were passed into a tall cylinder, the contents being protected from the air. In the first experiment, when there was an excess of trimethylamine, a white solid was formed. When this was removed it was found to be very hygroscopic. It had a strong odor of chlorine. It has not yet been possible to analyze it, but its conduct suggests that it is analogous to the products formed with bromine and with iodine. It is very easily decomposed by the action of moist air. Contact with water destroys the bromide. The iodide is decomposed by boiling water. In a second experiment there was for a time by mistake an excess of chloride. Under these circumstances the trimethylamine on entering the cylinder burned with a brilliant flame, and soot was deposited, showing a complete breaking down of the compound.

Action of Bromine on Dimethylamine.

Dimethylamine was found to take up two atoms of bromine in the same way as trimethylamine. The same product is formed by treating dimethylamine hydrobromide with bromine. Its properties are similar to those of the analogous compound obtained from trimethylamine. The results of the analyses are given below. In analyses I and II the compound formed by the action of bromine on the amine was used. In analyses III and IV that prepared by the action of bromine on dimethylamine hydrobromide was used :

I. 0.2392 gram salt gave 0.1875 gram total Br.
II. 0.2951 " " " 0.1147 " free Br.
III. 0.1989 " " " 0.1557 " total Br.
IV. 0.2351 " " " 0.0918 " free Br.

	Calculated for $(CH_3)_2HNBr_2$.	Found. I.	II.	III.	IV.
1 Atom Br	39.02	....	38.87	....	39.10
Total Br	78.04	78.38	....	78.23	....

Compounds Containing Two Different Halogen Atoms.

When the chloride of either dimethyl- or trimethylamine is treated with bromine a compound is formed containing both bromine and chlorine. It is probable that there is here also a substitution of bromine for halogen which, in the case of dimethylamine, would give the compound $(CH_3)_2HN.BrCl$. The reaction does not appear to be as clean as when bromine acts upon the bromides. An analysis was made of the product formed from dimethylamine hydrochloride, and, though the results were not satisfactory, they pointed to the formula above given.

The chlorides and bromides of both dimethyl- and trimethylamine react with iodine, forming compounds which give up their iodine in contact with water.

Action of Bromine and Iodine on Methylamine.

Methylamine hydrobromide was treated with bromine in the manner described in the case of trimethylamine. There was apparently no action. When the salt was freed from the excess of free bromine, it was found to be the unchanged hy-

drobromide. When free methylamine was conducted into bromine there was a rise in temperature and a solid substance was formed. When an attempt was made to filter off this compound, there was a slight evolution of gas. The compound proved to be methylamine hydrobromide, which must have been a secondary product.

The amine was passed into an alcoholic solution of iodine. No precipitate was formed. Evidently methylamine forms addition-products with the halogens with much greater difficulty than dimethyl- or trimethylamine.

The results above described show the existence of well characterized halogen addition-products of some of the substituted ammonias. The investigation has been temporarily interrupted, but, as already stated, it will be taken up in the near future.

ON SILICIDES.

(*Preliminary Note.*)

By G. de Chalmot.

Copper Silicide.—If a mixture of sand and charcoal is heated in an electric furnace in the presence of copper, silicides of copper are readily obtained. If an excess of sand and charcoal is used, a crystallized silicide can be obtained, which has probably the formula Cu_2Si_3. I have not thus far obtained entirely pure crystals, and have not found any means of purifying them. The purest specimen gave the following results:

	Calculated for Cu_2Si_3.	Found.
Cu	60.08	60.30
Si	39.92	38.62–38.82
Fe		0.64

The iron originated from the sand which had been used.

The silicide crystals are flat and of a brilliant bluish-white metallic appearance. The specific gravity of the impure crystals was 4.25. This silicide is much softer than iron or silver silicide. It does not scratch glass and can easily be pulverized. The crystals are attacked by *aqua regia*. A part of the copper is then dissolved and silica is formed. The crystals

are readily decomposed by a mixture of potassium and sodium carbonate and potassium nitrate.

If a mixture of silica, carbon, and lime (or any other flux) is subjected to a direct electric current of high amperage (240) and low voltage (20–30) and the cathode is made up of copper, a still larger percentage of silicon can be united with the copper. The mixture of sand, lime, and charcoal becomes liquid and is electrolyzed. I obtained in this way an alloy with 51.51 per cent. of silicon and 43.52 per cent. of copper. Larger amounts of calcium were also present.

Silicide of Silver.—By subjecting a mixture of sand, charcoal, lime, and pieces of silver to a current of 240 amperes and 25 volts I obtained a silicide of silver which, however, contains some calcium. This silicide is hard enough to scratch glass and rather tough. The color is grey. It is apparently homogeneous and crystalline. By boiling it with nitric acid ($1HNO_3 + 2H_2O$) for seventy-five minutes only a part of the silver was dissolved, and silica was formed at the same time. I therefore assume that the silicon and the silver are not simply mixed, but have entered into chemical union. This fact is of importance in so far as Moissan states[1] that silicon does not combine with silver, but is dissolved by it, and separates out when the mixture cools. In Moissan's experiments electrolysis was, however, excluded. My results agree with those of Warren.[2]

SPRAY, N. C., Dec. 7, 1895.

Contribution from the Laboratory of the University of California.

SOME OF THE PROPERTIES OF LIQUID HYDRIODIC ACID.

BY R. S. NORRIS AND F. G. COTTRELL.

In the first published account of the preparation of liquid hydriodic acid, it is described[3] as a yellowish liquid resembling liquid chlorine. The author prepared it by the action of sulphuretted hydrogen, iodine and water upon one another under strong pressure. Hydrogen persulphide, iodine and water were placed in separate bends in a stout glass tube

1 Compt. rend, **121**, 625. 2 Dammer's Handbuch für Anorg. Chemie, **2**, 825.
3 Kemp: Phil. Mag., 3rd Series, (1835), **7**, 444.

which was then sealed. When the hydrogen persulphide decomposed, the hydrogen sulphide which was formed acted upon the iodine, and the water was added to the product. The pressure exerted by the hydriodic acid formed under these conditions was enough to liquify it. None of its chemical properties were determined.

Faraday prepared it ten years later, in 1845, by subjecting gaseous hydriodic acid to the low temperature produced by solid carbonic acid.[1] He found that it attacked "hair, fat, and even the copper and mercury of the apparatus," and solidified at —51° C. to a clear colorless solid. No further determinations of its properties were made.

This is practically all the work that had been done on the liquid acid when we took up the investigation. What we have attempted to do is to determine its action upon some of the more common inorganic substances. We obtained the liquid hydriodic acid by the condensation of gaseous hydriodic acid by means of solid carbonic acid. The method of preparation of the gaseous hydriodic acid which we used was selected in preference to those generally described, on account of its easy manipulation and the small amount of water that came off with the acid. Since it might be used to good advantage for other purposes where an anhydrous acid is wanted, we will describe it in detail. Two grams of *dry* red phosphorus were placed in a quarter liter flask provided with a delivery tube. Twenty-four grams of iodine were then added gradually while the flask was gently warmed and shaken. The phosphorus triiodide thus formed was allowed to solidify, and when ready for use, ten cubic centimeters of water added to it. The reaction sometimes began on the addition of the water, but it was generally necessary to apply heat to start it, and to obtain all of the hydriodic acid from the solution quite a high heat was necessary. By properly regulating the heat it was possible to obtain the hydriodic acid free from iodine.

The hydriodic acid prepared in this manner was passed through a tube containing phosphorus pentoxide, then

[1] Faraday: Ann. Chim. Phys., 3rd Series, (1845), **15**, 257; and Ann. Chem. (Liebig), **56**, 154.

through a glass stoppered U-tube surrounded with ice to partially cool the gas, and then into the collecting tube, which was surrounded with solid carbon dioxide. The latter was obtained by holding a piece of flannel cloth over a tube connected with the nozzle of an inverted cylinder of liquid carbon dioxide and turning on the stop-cock. The tube in which the liquid hydriodic acid was to be collected was surrounded with the carbon dioxide thus obtained, which in turn was surrounded with several thicknesses of the woolen cloth. Under these conditions the carbon dioxide evaporated quite slowly.

In the first experiments the hydriodic acid was collected in glass tubes, which were sealed after the substance to be tested had been added. But it was found impossible to prevent the formation of a large amount of free iodine in the upper part of the tube in attempting to seal it off, and this altered the conditions of the experiments a great deal in some cases. We therefore discarded this arrangement and substituted tubes closed at one end, and furnished with ground glass stoppers. The hydriodic acid was collected in these in the same manner, the substance added and the tube closed with the stopper previously coated with vaseline. The tube was then removed from the carbon dioxide and placed in a wooden clamp, which held the stopper in place. By this means the liquid hydriodic acid could be kept at the ordinary temperature of the room for 2 to 3 hours before it all escaped.

The hydriodic acid which we obtained in this manner was a colorless limpid liquid, freezing to an ice-like solid of greater density than the liquid. The yellow color of the liquid hydriodic acid which Kemp described was due to some impurity, as out of over twenty samples of the acid which we prepared, using care to prevent the formation of free iodine, none of them had the slightest color. Sunlight decomposes it quite rapidly, setting iodine free, which dissolves in the liquid forming a reddish purple solution resembling the solution of iodine in carbon bisulphide. When such a solution is cooled down the purple color gradually fades until the liquid solidifies, when a light brown color appears, due probably to the solid iodine which has separated out. The action of

sunlight becomes less as the amount of free iodine in the solution increases. The prolonged action of sunlight was shown by the following experiment. A thin glass tube about 3 mm. in diameter was two-thirds filled with liquid hydriodic acid and sealed. It was placed in such a position that the sun could shine upon it about eight hours a day. The color of the solution became gradually deeper, and in about two weeks crystals of iodine began to separate out of the solution as it cooled during the night. When warm there were two distinct layers in the solution, the darker one beneath. At the end of two months the iodine that had separated out occupied about one-third of the whole volume. During the third month of exposure the tube disappeared, and we are unable to state what the final action of sunlight is, whether or not a state of equilibrium, due to the pressure of free hydrogen and to the amount of iodine present, would finally be established when no more decomposition would take place.

Action on the Metals.

In experiments with the metals care was taken to obtain the hydriodic acid as free from iodine and water as possible, and to use only the purest metals that we could obtain.

Silver.—The action on silver was quite rapid with the evolution of hydrogen and the formation of silver iodide, which dissolved slightly in the hydriodic acid.

Mercury.—A globule of mercury dissolved quite rapidly with evolution of hydrogen and formation of mercurous and mercuric iodides, as shown by the color. The former showed a slight crystalline structure, indicating that it had dissolved in the acid.

Lead.—The surface of a small piece of lead became dull, but further than this no action was noticed.

Copper.—Metallic copper dissolved slowly with the liberation of hydrogen and the formation of a crust of cuprous iodide on the surface of the metal. This experiment was one of the first made, where sealed tubes were used, and consequently there was free iodine present in the acid to start with. But the iodine was entirely removed by the copper, leaving a colorless solution.

Bismuth.—There was no apparent action on bismuth aside from the formation of a very slight red film on the surface of the metal.

Cadmium.—The only action on metallic cadmium was the formation of a slight tarnish on the surface of the metal, probably due to a small amount of free iodine dissolved in the hydriodic acid.

Tin.—There was no action on tin until the temperature of the solution rose to about 0° C. Above that temperature the action was rapid, but ceased again when the temperature was lowered. The metal dissolved completely with the formation of a yellow solution, from which crystals of stannous iodide deposited on the evaporation of the hydriodic acid. The crystals were difficultly soluble in water.

Arsenic.—There was no evolution of hydrogen from metallic arsenic, but the acid became yellow and left a crystalline deposit on evaporation. The surface of the metal did not tarnish.

Antimony.—In contact with metallic antimony the acid quickly assumed a reddish color and the surface of the metal became coated with a film. There was no evolution of hydrogen, but a slight reddish crystalline precipitate was deposited on the evaporation of the hydriodic acid. This fact can only be explained by the presence of some impurity in either the metal or the acid. It was probably due to a slight amount of the oxide with the metal and a trace of free iodine in the acid.

Iron.—Iron dissolved quite rapidly, forming a dark solution. A greenish black residue was left on the evaporation of the acid.

Aluminium.—Aluminium dissolved rapidly with a copious evolution of hydrogen. As the hydriodic acid evaporated crystals of aluminium iodide were deposited. When a drop of water was added to the crystals they were decomposed with a hissing sound, and evolution of heat, an insoluble grayish residue being left.

Zinc.—A thin gray film, slightly crystalline, was formed on the surface of a small piece of zinc, soon after it came in contact with the acid. But after remaining in the hydriodic

acid for several days in a sealed tube, no further action was found to have taken place. In contrast to the action of copper under the same conditions the zinc did not remove the free iodine from the solution.

Magnesium.—The acid had no effect on a piece of magnesium ribbon.

Sodium.—The action of the liquid acid on metallic sodium was rather slow at about the freezing-point of the former, but became very rapid as the temperature rose.

Potassium.—The action on potassium was more violent than on sodium. The metal was attacked very rapidly even at the melting-point of the hydriodic acid.

Boron and Silicon.—There was no apparent action on boron or on crystalline or amorphous silicon.

Thallium.—A yellowish film formed on the surface of a particle of metallic thallium, but otherwise there was no action.

Metallic Oxides.

Cupric Oxide.—Cupric oxide dissolved quickly with the liberation of iodine according to the following equation:

$$2CuO + 4HI = 2CuI_2 + 2H_2O$$
$$2CuI_2 = Cu_2I_2 + I_2.$$

Manganese Dioxide.—The action on manganese dioxide was rapid, iodine being liberated in abundance.

Carbonates.—Neither calcium carbonate nor dry sodium carbonate was acted upon in the slightest degree.

Non-Metallic Substances.

Sulphur.—A small piece of stick sulphur floated on the surface of the acid and gradually dissolved. As the experiment progressed, iodine was liberated, hydrogen sulphide being formed at the same time.

Carbon Disulphide.—The acid formed a homogeneous solution, but there was no further apparent reaction between them.

Water.—Water and liquid hydriodic acid do not mix, even when shaken together. A drop of water, when shaken with the acid, acted the same way as a drop of oil shaken with

water, *i. e.*, it broke up into globules, which rose to the surface.

Gases (Liquefied).

In these experiments small, sealed, thin glass tubes containing the various gases in liquid form were dropped into the tubes of liquid hydriodic acid, and the latter then placed in the clamp and shaken until the inner tube was broken. This was the most practicable means that suggested itself for bringing the two substances together in a liquid state at ordinary temperatures, although it had this disadvantage,—the intermediate reactions could not usually be seen on account of the rapidity and violence of the action.

Chlorine.—We were especially fortunate in the experiment with chlorine, a small hole being formed in the tube, which allowed the action to proceed slowly. Iodine was set free as soon as the chlorine came in contact with the acid. Some of the iodine penetrated into the chlorine tube, producing a yellow precipitate of iodine trichloride. As the chlorine issued from the tube it formed a yellow cloud, which, as the action became more energetic, burst into a flame. This increased the violence of the action so much that it caused the outer tube to explode.

Cyanogen.—When the tube containing the liquid cyanogen was broken, the two substances immediately combined with the liberation of iodine, formation of hydrocyanic acid, and of a flocculent precipitate. The latter was deposited as a reddish brown residue upon the evaporation of the hydriodic acid. We did not determine its composition.

Sulphur Dioxide.—Liquid sulphur dioxide reacted with the hydriodic acid setting free sulphur and iodine, and forming sulphuretted hydrogen. The sulphur was deposited in the form of a thin sheet of *yellow* plastic sulphur on the surface of the solution. When removed from the tube it gradually changed into the ordinary brittle form. The presence of hydrogen sulphide was easily detected by its odor upon opening the tube. Three experiments gave similar results. The probable reaction may be represented by the following equation:

$$10HI + 2SO_2 = 4H_2O + H_2S + 5I_2 + S_2.$$

Ammonia.—With liquid ammonia the reaction was violent and accompanied with a considerable rise of temperature. The two substances combined directly to form ammonium iodide.

Two experiments were made, with alcohol and ether respectively, which suggest some very interesting results to be obtained in the field of organic chemistry. Absolute alcohol and ether were each mixed with the liquefied acid. They both combined without any visible reaction to form a syrupy liquid, which separated into two layers, consisting of an aqueous solution of hydriodic acid and ethyl iodide respectively. The reactions may be represented thus:

$$C_2H_5OH + HI = C_2H_5I + H_2O;$$
$$(C_2H_5)_2O + 2HI = 2C_2H_5I + H_2O.$$

Some interesting points are brought out in regard to the difference between the properties of hydriodic and hydrochloric acid, by comparing the results of these experiments with those of similar experiments performed by Gore[1] with hydrochloric acid. There is this difference to be noted, however, in the two sets of experiments,—the above experiments have to do with *liquid* hydriodic acid alone, while in those of Gore on hydrochloric acid the action was generally an intermittent action of the liquid and gaseous acid; and there is no doubt that in some cases this altered the results of the experiments considerably.

None of the metals, except aluminium, were dissolved by liquid hydrochloric acid, and where there was any action it was probably due to the gaseous acid. Even sodium and potassium did not set hydrogen free from the liquid acid, but it is suggested by the author that the two metals may have been entirely converted into the chlorides by the gas before coming in contact with the liquid acid.

In opposition to this we find that liquid hydriodic acid acted upon half of the metals experimented with. Silver, mercury, copper, tin, iron, aluminium, sodium and potassium were attacked. Lead, bismuth, cadmium, arsenic, antimony, zinc, magnesium and thallium were unacted upon. These same metals, excepting mercury, were the ones used by Gore with the results mentioned.

[1] Phil. Mag. [4], **29**, 541.

Copper oxide and manganese dioxide were not dissolved by liquid hydrochloric acid; whereas they were both attacked by liquid hydriodic acid with the liberation of iodine.

There was no action on calcium carbonate (marble) by either of the acids; and, although sodium carbonate was converted into sodium chloride by the hydrochloric acid, this action was probably due to the hydrochloric acid gas, as no gas was liberated from the carbonate in contact with the liquid hydrochloric acid.

Sulphur was not attacked by liquid hydrochloric acid, but was dissolved by liquid hydriodic acid. Iodine was dissolved by both of them, forming a purple-red solution.

Comparing the action of liquid hydriodic acid with that of the gaseous form and its solution in water, the following points of difference are to be noted. Most of the metals are dissolved by the aqueous solution of hydriodic acid; among them lead, zinc and magnesium, which are not attacked by liquid hydriodic acid. Cyanogen forms with an aqueous solution of hydriodic acid, ethane, ammonia and oxalic acid,[1] and when the same solution is heated glycocol is formed.[2]

$$(CN)_2 + 5HI + 2H_2O = CH_2NH_2COOH + NH_4I + 2I_2.$$

The action is also complicated in the case of the liquid acid, but probably quite different from the above. Sulphur dioxide and hydriodic acid in the gaseous form and dry do not react,[3] but in solution[4] the action is similar to that which takes place between the two substances in liquid form, hydrogen sulphide, water, iodine, and probably sulphur iodide being formed.

The most striking points brought out by the experiments are the action of the acid on sulphur and its inertness toward the carbonates. The explanation which immediately suggests itself for the latter peculiarity is the want of contact between the two substances, or the formation of an impervious layer of carbon dioxide or of the iodide on the surface of the carbonate; but this is certainly untenable in the case of the similar action of liquid hydrochloric acid, or rather lack of action, on a *porous* piece of lime, as determined by Gore, so it

[1] Berthelot, Jsb., 1867, 347. [2] Emmerling: Ber. d. chem. Ges., 6, 1351.
[3] Soubeiran: J. Pharm., 13, 421. [4] Dammer: Anorg. Chem.

is at least a doubtful explanation in the case of the carbonates.

The conclusions to be drawn from the experiments and the comparisons which follow are that liquid hydriodic acid is in general more inert than gaseous hydriodic acid or its solution in water, and that it is less stable and more active than hydrochloric acid in the same form.

ON THE PREPARATION OF HYDROBROMIC AND HYDRIODIC ACID.

By J. H. Kastle and J. H. Bullock.

It is doubtful if any of the methods proposed for the preparation of these two acids have ever come into general use. That such is the case is shown by the fact that the whole treatment of the chemistry of these two acids is quite brief in even the better text-books and treatises on chemistry. And yet it is just by the aid of these compounds that the greatest knowledge can be gained concerning the chemistry of the halogen family; and it is through the study of these hydrogen compounds that we can make the most satisfactory comparison of chlorine, bromine, and iodine. If, for example, it can actually be shown the student, in the case of hydrochloric and hydriodic acids, that both of these substances are heavy colorless gases, which fume in the air, have powerful acid odors and dissolve in water with great readiness, forming strongly acid solutions, one of which remains unaltered under ordinary conditions—the other changing; and, further, that one of these compounds cannot be decomposed by heat alone, whereas the other can with the greatest ease; that one is readily attacked by oxidizing agents, the other not:—if these phenomena can actually be brought before the student, it is more than likely that he will have some clear conceptions as to the real resemblances and differences existing between chlorine and iodine. On the other hand, if he is shown a great deal about hydrochloric acid and little or nothing about the corresponding iodine compound, as is usually the case, he will probably quit the subject with no clear conceptions as to the nature of the latter compound; and in some instances he may even be troubled

with doubts as to its existence. And, further, if attractive and brilliant experiments are possible at all they are possible with just such unstable compounds as these.

Realizing the importance of having these unstable halogen acids at their disposal chemists have made quite a number of attempts to devise satisfactory methods for their preparation. Of the many methods which have been proposed for the preparation of hydrobromic acid, two are certainly worthy of notice as yielding good results. One of these, described by Erdmann,[1] consists in bringing bromine slowly into benzene containing a little ferrous bromide, and purifying the resulting hydrobromic acid gas by passing it through a tube containing ferric bromide and finally through one containing anthracene. The other method, that of Champion and Pellet,[2] consists in leading bromine into paraffin heated to 185° C.

It is believed, however, that the method herein proposed for making hydrobromic acid is simpler and better than either of the above for these reasons: First, the materials used are easy to obtain; secondly, no brominating agent is necessary; and thirdly, the formation of the hydrobromic acid gas proceeds regularly, smoothly, and rapidly without the aid of heat, and with little or no attention after the flow of bromine has been once regulated.

Of the methods proposed for the preparation of hydriodic acid, that involving the use of red phosphorus, iodine, and water seems to have come into most general use. The objection to this method is that, unless great precautions are taken in the beginning, explosions are liable to occur. Hence, it is believed that the method here recommended for the preparation of this acid has advantages over the old method involving the use of red phosphorus, for the reason that no precautions whatever need be taken in preparing the acid rapidly by the process here described.

Preparation of Hydrobromic Acid.

The method here proposed for the preparation of this acid takes advantage of the reaction between bromine and naphthalene. Any one who has ever had occasion to bring these two sub-

[1] Anleitung zur Darstellung chemischer Präparate: Erdmann.
[2] Compt. rend., 70, 620.

stances together has doubtless remarked the great ease with which they react upon each other. When brought together even at ordinary temperatures, torrents of hydrobromic acid gas are evolved. Therefore it occurred to one of us (Kastle) that this reaction might be employed in the preparation of hydrobromic acid. Such, indeed, has proven to be the case, the mode of procedure being as follows: About 15–20 grams of naphthalene are dissolved in a small quantity of ortho-xylene and the solution placed in a Florence flask of one-half to 1 liter capacity. The flask is connected, by means of a bent glass tube, with a double-neck Woulff's bottle, which is partially filled with a solution of concentrated hydrobromic acid[1] holding a small quantity of red phosphorus in suspension; and, in turn, is connected with a U-tube containing red phosphorus and one or more drying tubes partly filled with phosphorus pentoxide. Attached to the farther end of the drying tubes is a tube for the delivery of the dry hydrobromic acid gas. The bromine is introduced into the solution of naphthalene in the flask by means of a tap-funnel, the end of which dips beneath the surface of the liquid. On allowing the bromine to flow slowly into the solution of the naphthalene, action takes place at once, and hydrobromic acid is rapidly evolved. By passing the gas through the concentrated aqueous hydrobromic acid containing red phosphorus in suspension, it is deprived of any free bromine that may pass over along with it, (which, by the way, is never present in any considerable quantity) so that, after passing through the U-tube containing dry red phosphorus and the drying tubes, it is obtained as a perfectly colorless gas. With this simple apparatus, and working with the quantities given in the above, the acid can be prepared quite as rapidly as hydrochloric acid can be prepared from sulphuric acid and salt; and with no more trouble or attention, for the reason that, if the flow of bromine into the solution of the naphthalene be once properly regulated, the formation of the acid proceeds regularly and automatically.

[1] The object in using a concentrated solution of hydrobromic acid is that this solution allows all of the hydrobromic acid gas to pass through and, at the same time, dissolves and retains any free bromine better than water, thereby giving the red phosphorus a chance to combine with it.

In order to obviate the use of xylene, which is not always easily obtained, some experiments were tried, in which kerosene boiling above 150° C. was used as a solvent for the naphthalene. It was found to work just as satisfactorily as the purest orthoxylene. And, lastly, to put the method entirely within the reach of all lecturers upon chemistry, some experiments were tried with *moth balls*,[1] which were found to consist almost, if not entirely, of naphthalene, in the place of the pure naphthalene. This preparation, viz., the *moth balls*, was found to serve the purpose quite as well as the purest naphthalene, as will be seen from the following results :[2]

I. 50 grams of bromine, with 15 grams of naphthalene, dissolved in 50 cc. of orthoxylene, gave 21 grams of hydrobromic acid. Theory = 26 grams HBr.

II. 90 grams of bromine, with 15 grams of naphthalene dissolved in 50 cc. xylene, gave 33 grams of hydrobromic acid. Theory = 46 grams.

III. 105 grams of bromine, with 12.8 grams of naphthalene dissolved in 20 grams of xylene, gave 40.5 grams of hydrobromic acid. Theory = 53.5 gram HBr.

IV. 95 grams of bromine, with 12 grams of naphthalene (in form of *moth balls*) dissolved in a small quantity of kerosene, gave 47.5 grams of hydrobromic acid. Theory = 48.5 grams HBr.

V.[3] 95 grams of bromine, with 12 grams of naphthalene (in form of *moth balls*) dissolved in a small quantity of kerosene, gave 60.5 grams of hydrobromic acid. Theory = 48.5 grams of HBr.

In all there was obtained 202.5 grams of hydrobromic acid, thetheory being 222.5 grams for the quantity of bromine used ; a loss of only 9.1 per cent.

[1] As the name indicates, these *moth balls* are used for protecting clothing against moth. The preparation sold under that name in this part of the country has been found to consist almost, if not entirely, of naphthalene, and may be obtained at any drug store for 5 or 10 cents a pound.

[2] In the quantitative experiments the mixture of naphthalene and bromine was gently warmed towards the end of the reaction in order to drive off any small quantities of hydrobromic acid which might remain dissolved in the bromnaphthalene.

[3] That more than the theoretical quantity of hydrobromic acid was obtained in this experiment is accounted for by the fact that, during the operation, the wash-bottle containing the concentrated hydrobromic acid got quite hot, so that hydrobromic acid distilled over into the vessel in which the acid was finally collected.

In addition to these experiments, which were conducted with the view of finding out the quantity of hydrobromic acid set free, the method has been tried upon the lecture-table with entire success. The gas was collected, handled, and experimented with with the greatest ease. The method is certainly to be recommended for lecture-work and for the preparation of large quantities of the acid.

Preparation of Hydriodic Acid.

The method here proposed for the preparation of this acid depends upon a reaction first observed by Etard and Moissan,[1] viz., that, when iodine and common resin (colophony) are heated together, hydriodic acid is evolved. Not having access to the original papers of Etard and Moissan upon this subject, we are unable to judge from the abstract[2] whether it was ever proposed to utilize the reaction in the preparation of the acid, or whether it was simply their object to call attention to it as being one of the reactions of which iodine is capable. Be this as it may, it is certain that this simple mode of preparation of hydriodic acid has escaped the notice of American chemists; at least it has never come into general use; and hence it cannot be amiss to call attention to it with such modifications as have been found advantageous.

When a mixture of iodine and common resin, in about equal parts by bulk, is heated, hydriodic acid, together with small quantities of iodine, are evolved. The mixture foams considerably, however, and a black disagreeable liquid distils over. To obviate this and to render the hydriodic acid as pure as possible, the following method was tried successfully:

10 grams of finely divided iodine are mixed with an equal bulk of finely powdered resin and this mixture is then intimately mixed with a little more than an equal bulk of white sand. The mixture of iodine, resin, and sand is then placed in a small glass retort, the neck of which, accurately fitted with a cork, is connected with one of the necks of a double-neck Woulff's bottle, and extends for some distance into the Woulff's bottle. The other neck of the Woulff's bottle is connected with a U-tube containing red phosphorus. This U-

[1] Bull. Soc. Chim., **34**, 69. [2] Ber. d. chem. Ges., **13**, 1862.

tube in turn is connected with a calcium chloride cylinder, which is filled with alternate layers of glass-wool and phosphorus pentoxide, the calcium chloride cylinder being connected with a tube for the delivery of the gas.

On gently heating the retort containing the mixture of iodine, resin, and sand, hydriodic acid gas is freely evolved together with small quantities of iodine and the brownish liquid to which reference has already been made. Both of the latter are condensed in the Woulff's bottle, and, if any iodine escapes condensation at this point it is held back by the red phosphorus in the U-tube through which the gases next pass. On passing through the cylinder containing the phosphorus pentoxide, the hydriodic acid is dried completely, so that it may be collected in cylinders by displacement of air as a perfectly colorless gas. Without special precaution 5.4 grams of hydriodic acid were made from 10 grams of iodine by this method.

It should be said further that the method is a rapid one and in every way adapted to work on the lecture-table. The apparatus once set up and the mixture put in the retort, one can easily collect, in a few minutes, a sufficient quantity of the dry gas to illustrate its remarkable and beautiful properties. For example, the apparatus having been set up, the gas was prepared and collected in quantities sufficient for the following experiments, and the experiments themselves performed all in about a quarter of an hour:

1. Introduction of lighted taper into the gas.
2. Action of dry chlorine on gaseous hydriodic acid to show formation, first of iodine and then of iodine trichloride.
3. Decomposition of the gas into its elements by passing it through a heated tube.
4. Oxidation of the gas by fumes of nitric acid.
5. Absorption of the gas by water, and preparation of aqueous hydriodic acid.

In view of these results there can be no doubt as to the efficiency of this method of preparing hydriodic acid.

In conclusion, it may be said that both of the methods above described for these two acids are highly satisfactory. The materials used in the processes above described are such

as are easily accessible to all. There are no explosions attending the formation of these acids, nor is there any troublesome phosphonium bromide or iodide produced to clog up the apparatus, as is the case with the methods involving the use of phosphorus. The methods described in the above are rapid and practically free from the objections which may be urged against the other methods which have previously been proposed for the preparation of these two acids.

STATE COLLEGE OF KENTUCKY,
LEXINGTON, Dec., 1895.

Contributions from the Chemical Laboratory of Harvard College.

LXXXIX.—TURMEROL.[1]

BY C. LORING JACKSON AND W. H. WARREN.

Some years ago one of us, in conjunction with A. E. Menke, described a compound obtained from the oily extract of turmeric, to which the name of turmerol was given.[2] The present paper contains some additional work on this substance, which we are obliged to publish in an unfinished state because the departure of one of us from Cambridge prevents us from continuing the work together.

The turmerol at the time of its discovery was purified by distillation *in vacuo*, but the method used was a very imperfect one, because at that time no description of the best methods now in use had come to our notice, if indeed, they had been described at all. Accordingly, when we returned to the subject we felt it was necessary to revise this part of the work, and for this purpose applied to the tumerol the excellent method of fractional distillation *in vacuo* contrived by Anschütz, and soon found that the preparation studied by one of us and Menke was impure, and therefore that the formula of turmerol needed correction. Our analyses of a sample carefully purified and proved to be homogeneous by the analyses of different fractions led to the formula $C_{13}H_{18}O$ or $C_{14}H_{20}O$. We have been unable to determine which of these is correct, because the difference between them is only 0.25 per cent. for the carbon. This new formula agrees much better with the

[1] Presented to the American Academy of Arts and Sciences, October 12, 1892.

[2] This JOURNAL, 4, 368.

formulas of the oxidation products already obtained than that assigned to turmerol in the first paper on this subject.

The oxidation of turmerol with dilute nitric acid converted it into paratoluic acid, which was identified by its melting-point, 178°, the analyses of its calcium salt and anilide, and its conversion into terephthalic acid by further oxidation. This observation proves that turmerol contains a benzol ring with a methyl group attached to it, and a long side-chain of six (or seven) atoms of carbon in the para position to the methyl. In regard to the nature of the long side-chain we cannot speak with certainty, but it has been proved that one of the atoms of carbon in it is unsymmetrical, because turmerol shows circular polarization and that the atom of oxygen is attached to this side-chain. The earlier work of Menke and one of us further seems to indicate that turmerol is an alcohol,[1] and that it is oxidized by cold potassic permanganate with formation of acetic acid, carbonic acid, and two acids, $C_{11}H_{14}O_2$ (turmeric acid), and $C_{18}H_{12}O_4$? (apoturmeric acid).[2] We feel, however, that this earlier work needs revision before these points can be considered definitely settled, as the experiments on the alcoholic nature of turmerol are susceptible of an interpretation different from that given to them in the paper in which they were described, and the formula of apoturmeric acid is very doubtful. This revision will be undertaken in this laboratory, it is hoped, during the coming year.

Although it would be easy to assign a provisional formula to turmerol in accordance with the facts already observed, we have thought it wiser to postpone doing this until further investigation has given us a more secure foundation for such a formula.

Purification and Analysis of Turmerol.

The crude turmeric oil extracted from ground Bengal turmeric with ligroïn, as described in an earlier paper,[3] was heated to 150° under ordinary pressure for some time to remove as much as possible of the ligroïn, and then distilled under a pressure of 11–12 mm. according to the method of Anschütz, carrying the temperature to 200°. This separated it into a small lower

[1] This JOURNAL, **4**, 368. [2] *Ibid.*, **6**, 81. [3] *Ibid.*, **4**, 79.

fraction containing ligroïn, a larger one consisting principally of turmerol, and a viscous retort residue, which formed about one-half of the original oil. The large middle portion was repeatedly fractioned at a pressure of 11–12 mm., which divided it into a small lower fraction containing ligroïn, an insignificant retort residue, and the principal amount boiling from 158° to 163° under 11–12 mm. pressure. To test the purity of this substance it was distilled under the same diminished pressure once more, collecting the product in three fractions, the first and last very small in quantity, the middle one containing most of the substance, and these three fractions were then analyzed with the following results:

I. 0.3701 gram of the lowest fraction gave on combustion 1.1215 gram of carbonic dioxide and 0.3274 gram of water.

II. 0.4331 gram of the middle fraction gave on combustion 1.3071 gram of carbonic dioxide and 0.3802 gram of water.

III. 0.4795 gram of the highest fraction gave on combustion 1.4469 gram of carbonic dioxide and 0.4153 gram of water.

	Found.		
	I.	II.	III.
Carbon	82.64	82.28	82.30
Hydrogen	9.83	9.75	9.62

This experiment showed that the substance was not perfectly pure, since the lowest fraction contained more carbon than either of those which came over at higher temperatures. Accordingly the distillation at a pressure of 11–12 mm. was repeated, removing each time only a very small fraction which came over first, until this small lower fraction gave on analysis the same result as the portion left in the boiling-flask. This occurred after the third distillation, when the following results were obtained:

IV. 0.3408 gram of the small lowest fraction gave on combustion 1.0265 gram of carbonic dioxide and 0.2963 gram of water.

V. 0.3658 gram of the principal fraction gave on combustion 1.1041 gram of carbonic dioxide and 0.3175 gram of water.

	Found. IV.	V.
Carbon	85.13	82.28
Hydrogen	9.66	9.65

To these analyses we add another of an entirely different sample of turmerol.

VI. 0.5045 gram of the substance gave on combustion 1.5246 gram of carbonic dioxide and 0.4375 gram of water.

The percentages of carbon and hydrogen obtained from the analyses of pure turmerol are collected in the following table:

	II.	III.	IV.	V.	VI.
Carbon	82.28	82.30	82.13	82.28	82.39
Hydrogen	9.75	9.62	9.66	9.65	9.64

These results agree nearly with those calculated for the following formulas

	Calculated for $C_{13}H_{18}O$.	$C_{14}H_{20}$.
Carbon	82.10	82.35
Hydrogen	9.47	9.80

Of these we prefer the first, as this brings the calculated percentage of hydrogen below those found. On the other hand the percentages of carbon found are all a little too high for this formula, which may perhaps be due to the presence of a trace of ligroïn. It is evident that it is impossible to decide with certainty from these analyses which of these formulas is the correct one.

Properties of Turmerol.—The turmerol, after the purification described above, forms a yellowish oil, with a peculiar rather agreeable odor. It is decomposed partially by distillation at ordinary pressure, but under a pressure of 11–12 mm. it distils unchanged between 158° and 163°. Its specific gravity at 24°, referred to water at 4°, is 0.9561. Turmerol acts upon polarized light, turning the ray toward the right, with the following specific rotation for sodium light:

$$[a]_D = 24.58°.$$

It mixes easily with the common organic solvents, but is insoluble in water.

Oxidation of Turmerol with Nitric Acid.

In a previous paper[1] one of us with A. E. Menke showed

[1] This JOURNAL, 6, 81.

that turmerol, when oxidized in the cold with potassic permanganate, gave in addition to carbonic dioxide and acetic acid two new acids, to which the names turmeric acid and apoturmeric acid, and the formulas $C_{11}H_{14}O_5$ and $C_{15}H_{12}O_4$ (?) were assigned. As in this work the characterization of the apoturmeric acid was far from satisfactory owing to the very small yields and the unmanageable nature of these acids and their salts, and as we hoped by further study of these substances to throw light on the constitution of turmerol, we took up this part of the subject again. Since the preparation and purification according to the methods used in the earlier work were tedious in the highest degree, we tried the action of dilute nitric acid on turmerol in the hope that this might lead us more quickly to the desired result. This did not prove to be the case, but the product obtained was quite as important as the two acids we had hoped to get.

We proceeded as follows. A convenient quantity of turmerol was boiled with nitric acid (one part of acid of 1.38 specific gravity diluted with two parts of water) under a reverse condenser for some time. The yellow solution was filtered hot, and on cooling deposited a white crystalline substance, which sublimed very easily at a little over 170°. It was purified by sublimation, followed by warming with tin and hydrochloric acid to remove any nitro compound which might have been formed; after this it was crystallized from boiling water until it showed a constant melting-point, which stood at 178°. This at once suggested that the substance was the paratoluic acid $CH_3C_6H_4COOH$, which melts according to Beilstein and Yssel[1] at 176° to 177°, according to Fischli[2] at 180°. To confirm this inference we analyzed the calcium salt with the following results:—

I. 0.1106 gram of the air-dried salt lost 0.0165 gram when dried at 140°.

II. 0.1212 gram of the air-dried salt lost 0.0176 gram when dried at 140°.

	Calculated for $(C_8H_7O_2)_2Ca.3H_2O$.	Found. I.	II.
Water	14.83	14.92	14.52

[1] Ann. Chem.. (Liebig), **137**, 302. [2] Ber. d. chem. Ges., **12**, 615.

0.2848 gram of the calcium salt dried at 140° gave 0.1246 gram of calcic sulphate.

	Calculated for $(C_8H_7O_2)_2Ca$.	Found.
Calcium	12.90	12.86

The amount of water found (three molecules) corresponds to that obtained by Beilstein and Yssel[1] in the calcium salt of paratoluic acid. We also converted the acid into its anilid by treating it successively with phosphoric pentachloride and aniline. This after repeated crystallization from dilute alcohol melted constant at 143°, and gave the following result on analysis:—

0.1122 gram of the substance gave 7 cc. of nitrogen at a temperature of 29° and a pressure of 753.7 mm.

	Calculated for $C_8H_7ONHC_6H_5$.	Found.
Nitrogen	6.63	6.75

Here again the analysis gave the desired result, but our anilid melted at 143°, whereas according to Fischli[2] the anilid of paratoluic acid melts at 139°, according to Brückner[3] at 140–141°; we felt, therefore, that further proof of the para position of the side-chains in our acid was necessary, and this we obtained by the oxidation of the acid with potassic dichromate, according to the directions given by Beilstein and Yssel. For this purpose 0.5 gram of our acid was boiled in a flask with a return condenser with four parts of potassic dichromate, and an excess of sulphuric acid diluted with twice its volume of water, until there was a copious white precipitate; this was then filtered out, boiled three times with water and the residue converted into its dimethylester, which melted at 140–141°, thus proving that the product was terephthalic acid, and that our acid was paratoluic acid. We may add that a certain amount of the terephthalic acid was always obtained with the paratoluic acid when we oxidized turmerol with dilute nitric acid.

Some unsuccessful attempts to make derivatives of the turmeryl chloride, which was described in a previous paper,[4] may be mentioned here. The chloride was made by heating phos-

[1] Ann. Chem. (Liebig), **137**, 302. [2] Ber. d. chem. Ges., **12**, 615.
[3] Ann. Chem. (Liebig), **205**, 132. [4] This JOURNAL, **4**, 371.

phorus trichloride with turmerol for three hours. The product was purified by washing its ethereal solution with dilute sodic hydrate and water, drying with calcic chloride and distilling off the ether. It formed a dark oil, with a smell very different from that of turmerol, but as it decomposed, even when distilled at a pressure of 12 mm., no attempt was made analyze it again. In the hope of obtaining an aldehyde or ketone from it, 10 grams of the chloride was boiled with an aqueous solution of plumbic nitrate. Some plumbic chloride was formed, but the quantity of the chlorine removed was only 0.2363 gram, whereas the amount calculated for the complete reaction was 1.868 grams; we obtained therefore only 12.65 per cent. of the calculated amount, and, as the reaction was so incomplete, it was not surprising that we were unable to isolate the organic product. We also tried the action of potassic phthalimide on the turmerylchloride in the hope of getting turmerylamine, but found there was no action at 100°, little or none at 150°. From these results it is evident that turmerylchloride is not a very reactive substance.

XC. CERTAIN BROMINE DERIVATIVES OF RESORCINE.[1]

By C. Loring Jackson and F. L. Dunlap.

The research described in the following paper was suggested by the observation[2] that tribromnitroresorcine diethylether, when heated with a solution of sodic ethylate, lost two atoms of bromine, which were replaced by two of hydrogen, so that $C_6Br_3NO_2(OC_2H_5)_2$ was converted into $C_6BrH_2NO_2(OC_2H_5)_2$. Considering the easy removal of these two atoms of bromine, it seemed possible that the tribromresorcine diethylether, which differs from it only in the absence of the nitro group, might behave in a similar way. This expectation has not been fulfilled, as our experiments have shown that tribromresorcine diethylether does not give up bromine to sodic ethylate at the boiling-point of alcohol, and that the dibrom ether is not attacked below 200°, and therefore is, if anything, more stable than the symmetrical tribrombenzol, which according to Blau[3] is slowly con-

[1] Presented to the American Academy of Arts and Science, February 14, 1894.
[2] This Journal, 15, 641.
[3] Monatsh. f. Chem., 7, 630.

verted into dibromanisol at temperatures of 120° to 130°. The behavior of free tribromresorcine was next studied, and it was found that bromine could be removed with great ease, even water at its boiling-point decomposing this substance, while solutions of sodic carbonate, or sodic hydrate, or sodic ethylate dissolved in alcohol acted even more readily. These results show that the ethoxyl groups do not loosen the attachment of the bromine atoms to the benzol ring, whereas the hydroxyl groups have as much of this loosening effect as do the nitro groups in tribromdinitrobenzol.

We have not succeeded in determining the nature of the organic compounds produced by removing bromine from tribromresorcine, as they were brown amorphous bodies, which could not be brought into a state of undoubted purity for analysis. From their properties, however, it can be inferred that they are substituted resorcine ethers formed by a reaction involving the hydroxyl groups of the tribromresorcine. Sodium malonic ester gave a similar unmanageable product with tribromresorcine, bnt in addition to this acetylenetetracarboxylic ester was isolated. This substance could hardly be formed here otherwise than by the action of brommalonic ester on sodium malonic ester, and the brommalonic ester must have been formed by the replacement by hydrogen of one or more atoms of bromine in the tribromresorcine. It follows, therefore, that in this respect also the two hydroxyl radicals behave like the two nitro groups in tribromdinitrobenzol, in which a similar replacement of bromine by hydrogen has been observed when this substance is treated with sodium malonic ester.

The tribromresorcine diethylether melts at 68°–69°, and is formed by the action of an excess of bromine on the dibromresorcine diethylether, melting-point 99°–100°. This latter substance is prepared by the addition of bromine to a solution of resorcine diethylether in glacial acetic acid. The tribrom product was shown to have the bromine atoms in the symmetrical position to each other by treatment with nitric acid, which converted it into the tribromnitroresorcine diethylether melting at 101°, which is made from symmetrical tribromtrinitrobenzol.[1] The action of nitric acid on dibromre-

[1] This Journal, 15, 618.

sorcine diethylether was entirely different, as the product was a new dinitroresorcine diethylether melting at 126°, formed by the replacement of the two atoms of bromine by two nitro groups. A similar replacement of bromine by nitro groups was observed when the tribromresorcine was treated with fuming nitric acid, the product being the bromdinitroresorcine described by Typke[1] and Fèvre.[2] As this substance was obtained by the latter from dibromnitroresorcine, in this case also bromine was replaced by a nitro group, and several other cases are to be found in the chemical literature although they are far from common.

The most important point established by the observations given above is that in these cases hydroxyl or ethoxyl radicals have the same effect upon bromine which they have upon hydrogen attached to the benzol ring; for just as phenols are much more susceptible to the replacement of their hydrogen by halogens or nitro groups than the corresponding hydrocarbons, so the bromine can be replaced by other radicals, including the nitro group, much more easily in tribromresorcine than in tribrombenzol; while on the other hand the phenol ethers hold their hydrogen or bromine as firmly as the corresponding hydrocarbons. The one exception we have met with to this statement is the action of nitric acid upon dibromresorcine diethylether, in which the bromine is replaced by nitro groups, so that in this case the ether behaves like the free tribromresorcine rather than like the corresponding tribrom ether. This exception is the more remarkable, because we have found that toward other reagents, such as sodic ethylate, this dibrom ether shows the same great stability which characterizes the tribromresorcine diethylether.

As we could not remove the bromine from the tribromresorcine diethylether with sufficient ease, and the free tribromresorcine, although it gave up its bromine easily, gave unmanageable products since the hydroxyl groups took part in the reaction, we undertook the study of the tribromresorcine diacetate, which we hoped might give products that could be purified and analyzed; but these experiments did not lead to the desired result, as the acetate was converted into tribrom-

[1] Ber. d. chem. Ges., 16, 555. [2] Bull. soc. chim., 39, 591.

resorcine by the reagents used, even boiling with water producing this effect to a slight extent, and consequently the products were those already mentioned as obtained from this substance. When treated with fuming nitric acid, the diacetate gives tribromnitroresorcine diacetate which melts at 161°.

The sodium salt of tribromresorcine was also studied. This was obtained in white crystals by precipitating an ethereal solution with alcoholic sodic ethylate, and seemed to contain two molecules of alcohol of crystallization. It was remarkable on account of its slight stability, as even *in vacuo* or in an atmosphere of hydrogen after standing for a short time it suddenly turned black, when there was a considerable evolution of heat, and alcohol vapor was given off. The black residue gave up sodic bromide to water, and also a black soluble salt, while a red product was left behind. The black salt on the addition of acid gave a red precipitate similar to the product insoluble in water, but we were unable to bring either of these red amorphous substances into a condition undoubtedly fit for analysis; and although some analyses led to a very probable formula and reaction for the decomposition we can give no weight to these results, as we have no proof that the samples analyzed were homogenous. There is no question that these substances are very similar to the products obtained from tribromresorcine and sodic ethylate or carbonate.

Dibromresorcine Diethylether, $C_6H_2Br_2(OC_2H_5)_2$.

Resorcine diethylether, prepared by Pukall's method,[1] was dissolved in glacial acetic acid and bromine added to it until no more was taken up and a yellow color appeared in the solution. Crystals were soon seen to separate, and these were recrystallized from alcohol until they showed a constant melting-point, when they were dried in a desiccator and analyzed with the following results:

I. 0.2262 gram substance gave, according to the method of Carius, 0.2644 gram of argentic bromide.

II. 0.2272 gram substance gave 0.2628 gram of argentic bromide.

	Calculated for $C_6H_2Br_2(OC_2H_5)_2$.	Found. I.	II.
Bromine	49.38	49.74	49.22

[1] Ber. d. chem. Ges., **20**, 1141.

Properties.—The dibromresorcine diethylether crystallizes in white silky long slender prisms terminated by one plane nearly at right angles to the sides; they melt at 99–100°, and are slightly soluble in hot water; readily soluble in ether, benzol, and carbonic disulphide; very soluble in acetone and chloroform; also soluble in ligroïn. Alcohol is the best solvent to use in purification.

In a sealed tube at 100° sodic ethylate does not react with dibromresorcinediethylether, nor was any action observed until the tube was heated to 200°, when, upon distillation of the product with steam, a few oil drops passed over. This experiment shows that the dibromresorcine diethylether is no more reactive than symmetrical tribrombenzol, if in fact as much so, since Blau has converted this latter substance, by heating it at 120–130° with sodic methylate, into dibromphenol and its methyl ether.[1] As the interest in this work lay in the study of the effect of other radicals on the atoms of bromine rather than in the nature of the compounds formed, it was not thought worth while to spend the time necessary to prepare the product in quantity sufficient for its identification.

Dibromresorcine diethylether does not react with aniline in a sealed tube at temperatures ranging from 150–175°, and sodic phenylate at 230° also seems to have no effect upon it. It cannot therefore be called a very reactive substance.

Tribromresorcine Diethylether, $C_6HBr_3(OC_2H_5)_2$.

The crystals of dibromresorcine diethylether were treated with an excess of bromine, and then heated upon a steam-bath until the excess of bromine had evaporated. The reddish oil which resulted soon solidified and was recrystallized from alcohol until it showed the constant melting-point of 68–69°, when it was dried in a desiccator and analyzed.

0.2222 gram substance gave by the method of Carius 0.3177 gram of argentic bromide.

	Calculated for $C_6HBr_3(OC_2H_5)_2$.	Found.
Bromine	59.55	59.70

This body crystallizes beautifully in long pearly fibers, often collected in bunches and sometimes branched, which melt at 68–69° and are practically insoluble in cold water; very soluble in benzol and carbonic disulphide; readily soluble in

[1] Monatsh f. Chem., 7, 630.

ligroïn and chloroform; rather soluble in acetone, but less soluble in ether. Alcohol is the best solvent for purification.

This tribrom ether reacts but very slightly with sodic ethylate at the boiling temperature of alcohol, and no more strikingly when boiled with sodic amylate. When boiled with aniline, the tribrom ether gave an amorphous black mass from which nothing definite could be obtained. Inasmuch as the sodic ethylate had so little action on this body, it was deemed unnecessary to carry this line of work further, for the reasons given under the dibrom compound.

Constitution of Tribromresorcine Diethylether.

Tribromresorcine diethylether dissolves readily in fuming nitric acid, giving the body $C_6Br_2NO_2(OC_2H_5)_2$, as was proved by its melting-point, 100–101°. As Warren[1] and one of us prepared this substance from symmetrical tribromtrinitrobenzol, this experiment proves the symmetrical position of the three bromine atoms in tribromresorcine diethylether.

Dinitroresorcine Diethylether, $C_6H_2(NO_2)_2(OC_2H_5)_2$.

When dibromresorcine diethylether is treated with fuming nitric acid, the result is different from that obtained with the corresponding tribrom compound. To study this action, some of the dibrom ether was added to an excess of fuming nitric acid, when it immediately dissolved, after which it wast reated with excess of water and the reddish oil which separated allowed to solidify. It was then recrystallized from alcohol until it showed the constant melting-point of 126°, after which it was dried at 100° and analyzed.

0.1313 gram of the substance gave 13.5 cc. of moist nitrogen at a temperature of 26° and a pressure of 746.6 mm.

	Calculated for $C_6(NO_2)_2H_2(OC_2H_5)_2$.	Found.
Nitrogen	10.94	11.19

Properties.—The dinitroresorcine diethylether crystallizes from alcohol in radiated clusters of long white needles, or of smaller curved needles forming woolly masses. It is of a very faint yellow color and melts when pure at 126°. It is readily soluble in chloroform or acetone; slightly soluble in

[1] This JOURNAL, 15, 618.

ligroïn; soluble in benzol; tolerably soluble in carbonic disulphide; soluble also in ether. Alcohol is the best solvent for purification.

Tribromresorcine, $C_6HBr_3(OH)_2$.

Tribromresorcine was prepared by the method of Benedikt,[1] as this yields better results than the treatment of resorcine dissolved in water with bromine, used by Hlasiwetz and Barth.[2] For this purpose the calculated amount of bromine is run into a solution of resorcine in cold glacial acetic acid. After the addition of the bromine this solution is somewhat warm, and upon cooling a finely crystallized product separates, which is best washed free from acetic acid by decantation. If more than the calculated amount of bromine is added, pentabromresorcine is formed in addition to the tribromresorcine. The yield by this method is slightly over 57 per cent. of the theoretical.

A great many conflicting statements occur in the chemical literature regarding the melting-point of tribromresorcine. Hlasiwetz and Barth, who discovered it, give no melting-point. Typke,[3] in some work on tribromdioxyazobenzol, obtained a body with a constant melting-point of 104°. The amount of this body that he had was too small for analysis, but a careful comparison of its properties, especially its melting-point, its crystalline form, and its solubility, with that of tribromresorcine he had prepared himself, convinced him of the identity of the two substances.

Rudolph Benedikt[4] by the action of tin and hydrochloric acid upon Stenhouse's pentabromresorcine, obtained tribromresorcine which melted at 111°. He also gives analyses which agree very well indeed for the body in question.

Von Pechmann,[5] three years later, obtained a body by the action of an excess of bromine upon benzolresorcinephthaleïn, which he called tribromresorcine on the ground of the melting-point of 103°. He gives no analysis of this body, notwithstanding the fact that Benedikt had previously found its melting-point to be 111°.

[1] Monatsh f. Chem., **4**, 227. [2] Ann. Chem. (Liebig), **130**, 357.
[3] Ber. d. chem. Ges., **10**, 1578. [4] *Ibid*, **11**, 2168.
[5] Ber. d. chem. Ges., **14**, 1061.

Beilstein in his "Handbuch" gives only Typke's melting-point of 104°.

All of the tribromresorcine we have made use of in this research melted at 111°, the point given by Benedikt, and repeated recrystallization from water, which seems to be preferable to all other solvents, failed to raise its melting-point higher.

According to Hlasiwetz and Barth,[1] tribromresorcine when recrystallized from water contains water of crystallization, which it loses at 100°. As the presence of water of crystallization might explain the difference in the melting-points given by previous observers, we examined the tribromresorcine in this direction. Some of it was crystallized from hot water and dried in the air to a constant weight. This air-dried salt, which remained constant in a desiccator over calcic chloride, was heated to 100° for ten hours, when 0.2169 gram of the substance lost but 0.4 milligram in weight. Therefore tribromresorcine when recrystallized from water does not contain water of crystallization which it loses at 100°, as Hlasiwetz and Barth state.

In the recrystallization of the tribromresorcine from hot water, especially from boiling water, it was noticed that the crystals had a light pink color, so a study of the action of boiling water upon this body was taken up. One gram of the pure tribromresorcine was boiled in a 500 cc. flask, fitted with an inverted condenser, with 250 cc. of water. The greater part of the solid went into solution, and after the boiling had proceeded but a very short time the liquid became pink in color, which deepened into a dark red after the action had been carried on for twenty-four hours. The portion of the tribromresorcine which did not go into solution melted under the boiling water, its color also changing from a pink to a very dark red after the boiling had been continued for some time. At the end of twenty-four hours' boiling, we found that all of the tribromresorcine had not been changed into the red body, for on cooling crystals of a light pink color separated from the solution, which had the melting-point of 111°. Even further boiling, it seemed, failed to complete the change. Upon the

[1] Ann. Chem. (Liebig), **130**, 357.

addition of argentic nitrate to this solution, a heavy precipitate of argentic bromide was obtained, showing that bromine had been removed from the tribromresorcine.

The red body which formed the organic product in the reaction was amorphous, and could not be recrystallized from any solvents we could find.

It was thought that possibly in a sealed tube the reaction would run much more smoothly, converting all the tribromresorcine into the amorphous red body. Consequently, quite a number of experiments were tried with varying amounts of the substances, heated from twelve to twenty-five hours at different temperatures, but without success. The tribromresorcine, it seems, is incapable of complete transformation into the red body at temperatures below 200°, while at 200° it is carbonized after heating for a short time. As the solubilities of the red body are practically the same as those of the tribromresorcine, all methods for purification failed, and it could not be brought into a state fit for analysis. It is probable, however, that it contains more hydroxyl groups than the tribromresorcine, forming perhaps in the first place a substituted pyrogallol, (for in alkaline solutions the red body immediately blackens,) which is afterwards converted into more complex substances by reactions in which the hydroxyls bear a part.

Aniline or sodic alcoholates also acted easily with the tribromresorcine, but although much bromine was evidently removed in the form of hydrobromic acid or sodic bromide, in no case could any organic product be isolated in a state fit for analysis.

Sodium Salt of Tribromresorcine, $C_6HBr_2(ONa)_2.2C_2H_5OH$.

This salt cannot be obtained from an aqueous solution, although it seemed to be formed, since upon treating tribromresorcine with a dilute solution of sodic carbonate carbonic dioxide was evolved, but the solution at once turned black and evidently underwent a deep-seated change. The following method for obtaining it was accordingly adopted. One gram of pure tribromresorcine was dissolved in absolute ether, and to this was added less than the calculated amount of sodium dissolved in absolute alcohol (the calculated amount

of sodium is 0.13 gram). A precipitate immediately separated, consisting of short flat prisms having a silky luster. These were filtered off and thoroughly washed with absolute ether. In the preparation of this body, the ether must be in large excess; if the reverse was true (that is, if the absolute alcohol were in excess) no precipitate was formed. The crystals were transferred, after washing with absolute ether, to a desiccator and allowed to dry in a stream of hydrogen. Some of the salt thus prepared was submitted to analysis. All the operations with this substance must be carried on as quickly as possible, since it has a strong tendency to decompose, forming a black mixture, and this change takes place even *in vacuo* or in an atmosphere of hydrogen, although not so quickly as when in contact with the air. Even during the weighing in a closed tube, the substance often decomposed, but the following analyses were made with the unchanged substance, although in all the analyses made the samples used were light brown in color, showing that slight decomposition had taken place.

I. 0.1357 gram of the salt gave 0.0396 gram sodic sulphate.

II. 0.1398 gram of the salt gave 0.0416 gram sodic sulphate.

	Calculated for $C_6HBr_3(ONa)_2.2C_2H_5OH$.	Found. I.	Found. II.
Sodium	9.52	9.45	9.64

These results indicate that the salt contained two molecules of alcohol of crystallization, and that alcohol was present in the body was evident, for a great many times, in attempting to weigh it, the contents of the weighing tube would suddenly turn black, giving off heat, while a liquid collected in large drops on the sides of the tube, which was recognized as alcohol.

Properties.—The sodium salt of tribromresorcine crystallizes in short flat prisms of a white color and a silky luster. Its most striking property is its great instability, decomposing rapidly with the elimination of alcohol, the salt becoming black in color; when dissolved in water, the solution immediately turns black. A freshly prepared lot of this sodium salt was divided into two portions, one of which was put into a small tube through which a rapid stream of hydrogen was

passing, the other was put into a test-tube which was surrounded by a freezing-mixture of salt and ice, the substance in the test tube being in contact with the air. It was found that the sodium salt in the stream of hydrogen (at ordinary temperature) blackened more rapidly than did the salt which was in the freezing-mixture in contact with the air. This experiment proves that the salt is more stable in the cold than at ordinary temperatures, and also that the blackening is not due to oxidation. Since then we had proved that this behavior was not due to oxidation, it seemed possible that the black mixture obtained by drying at 100° might have the same percentage composition as the dried salt. Accordingly the amount of sodium was determined in a specimen of the salt which had been allowed to blacken and dried to a constant weight of 100°. The black body is slightly hygroscopic, so it must be weighed in a weighing tube.

0.2052 gram of the substance gave 0.0722 gram of sodic sulphate.

	Calculated for $C_6HBr_3(ONa)_2$.	Found.
Sodium	11.76	11.40

An attempt to determine the amount of alcohol present by heating some of the freshly prepared salt to 100° gave the following results :—

	Calculated for $C_6Br_3H(ONa)_2.2C_2H_5OH$.	Found.
Alcohol	19.05	17.97

This determination, although one per cent. too low, is as near as we could expect it to come, inasmuch as it was impossible to obtain a sample for analysis which was perfectly white ; but there is a more serious objection to this result and the determination of the sodium in the salt dried at 100°, as we have no proof that alcohol was the only substance volatilized during the decomposition and subsequent drying. In fact the determinations of the amount of sodic bromide contained in the dried mixture indicated that a certain quantity of hydrobromic acid might have been evolved. The only analyses of the salt, therefore, which are above suspicion, are those first given of the white undecomposed preparation.

The following experiments were tried to prove the nature of this decomposition of the salt. When the black decomposition product was dissolved in water, and dilute sulphuric acid added, a flocculent reddish brown precipitate was formed, which very much resembled ferric hydrate in appearance. The clear filtrate from this gave a very heavy precipitate of argentic bromide upon addition of argentic nitrate. This shows that the decomposition was produced by the elimination of a portion of the bromine from the ring. The amount of sodic bromide formed during the reaction was determined by treating the blackened salt with water of varying temperatures and for different lengths of time, and then the solutions were acidified with dilute sulphuric acid, the precipitate filtered off, and bromine determinations made in the clear filtrates. The results obtained were not constant, varying from 32.01 per cent. to 37.90 per cent. of bromine, and this variation may be explained by the supposition that a certain amount of hydrobromic acid escaped during the decomposition.

The study of the red flocculent precipitate obtained by the the addition of sulphuric acid to an aqueous solution of the sodium salt of tribromresorcine has not led to any trustworthy results. Treatment with water and ether showed that it was not homogeneous, and the different fractions thus obtained could not be brought into a state fit for analysis, as no means of proving that they were pure could be found. Some analyses of these fractions gave numbers agreeing fairly well with the very probable formula $[C_6H_2BrOH]_2O_2$; but for the reason just given it is impossible to accept this formula as established by them.

Tribromresorcine when treated with aqueous sodic carbonate dissolves with the evolution of carbonic dioxide, the solution immediately blackening, as has been stated already; upon acidification with dilute sulphuric acid a reddish brown flocculent precipitate was formed similar to that mentioned above, as the clear filtrate from this body gave a very heavy test for bromides. That in this case the blackening was not due to oxidation was shown by the fact that it took place in an atmosphere of hydrogen, even when the solution had been

boiled to insure the absence of dissolved oxygen. Sodic or potassic hydrate has the same effect upon tribromresorcine as the carbonate. The red precipitate obtained upon acidifying has not yet been obtained in crystals, and when heated decomposed without melting, giving off hydrobromic acid. This body is doubtless the same as that obtained by the action of water on tribromresorcine, and also from the blackened sodium salt by acidifying its aqueous solution, as has been described above.

Action of Sodium Malonic Ester on Tribromresorcine.

This reaction was taken up to see if another case of the peculiar substitution of bromine by hydrogen, already noticed by one of us,[1] could be obtained. After a great many trials the best mode for studying the reaction was found to be as follows. Five grams of sodium were dissolved in 250–300 cc. of absolute alcohol, and to this were added thirty-five grams of malonic ester. Twenty-five grams of tribromresorcine were then added, and this turned dark and afterwards dissolved. After boiling the mixture for three hours in a flask fitted with an inverted condenser, the alcohol was distilled off and the contents of the flask were acidified with dilute sulphuric acid. A dark red oil separated, which was dissolved in ether, this solution was then dried over calcic chloride and the ether distilled off. Upon standing several days, the residual oil turned rather viscous, and crystals were seen permeating the mass. These crystals may be obtained by absorbing the oil with bibulous paper or by distilling *in vacuo*. By crystallization from dilute alcohol the constant melting-point 76° was obtained, and as the crystals are white, contain no bromine, and their solubility, mode of crystallization, and shape correspond with those of acetylenetetracarboxylic ester, there can be no doubt that they are this substance. This acetylenetetracarboxylic ester could hardly have been formed otherwise than by the action brommalonic ester on sodium malonic ester, and the brommalonic ester it would seem must have been produced by the interchange of a bromine atom of the tribromresorcine with one of the atoms of hydrogen of the malonic ester. It follows

[1] This JOURNAL, **11**, 93, and **12**, 7.

from this reasoning, therefore, that we have here another case of the curious replacement of bromine by hydrogen, so often observed in this laboratory, and that the two hydroxyl groups of the resorcine exert the same action on one or more of the atoms of bromine as the two nitro groups in the tribromdinitrobenzol. The following fruitless attempt was made to isolate the other organic derivative formed. If the red oil absorbed by the bibulous paper, after the acetylenetetracarboxylic ester has been separated as completely as possible, be treated with benzol, it is divided into a soluble and an insoluble portion. The insoluble portion, by precipitating an alcoholic solution of it with benzol, came down in a flocculent form, and when dry was light brick-red in color. It was evidently closely related to the substance obtained by the action of water or sodic carbonate on the tribromresorcine, and like that could not be purified.

Action of Nitric Acid on Tribromresorcine.

Fuming nitric acid reacts easily with tribromresorcine. The product was recrystallized from benzol and upon analysis gave the following results:—

0.2219 gram of the substance gave by the method of Carius 0.1479 gram of argentic bromide.

	Calculated for $C_6HBr(NO_2)_2(OH)_2$.	Found.
Bromine	28.67	28.37

This analysis and the melting-point, 192°–193°, show the body to be one heretofore described by Typke[1] and Fèvre.[2]

We have found, in attempting to prepare the diacetate of dinitrobromresorcine, that dinitrobromresorcine would not react with acetyl chloride when heated with it at 100° for six hours in a sealed tube. Water does not react with dinitrobromresorcine in a sealed tube at temperatures varying from 100° to 120°. At temperatures between 150° and 190° the body is entirely decomposed, leaving a reside in the tube which seemed to be carbon, as it was insoluble in all solvents. It is strange that this substance should be less affected by water than the tribromresorcine, which is slowly acted on by water at its boiling-point. The dinitrobromresorcine reacts with sodic

[1] Ber. d. chem. Ges., 16, 555. [2] Bull. soc. chim., 39, 591.

ethylate, but, as in the case of the tribromresorcine, the resulting amorphous mass could not be purified or crystallized.

Behavior of Tribromresorcine Diacetate.

While the tribromresorcine itself reacts easily with boiling water and sodic ethylate, but gives unmanageable products, and the di- and tribromresorcine diethyl ethers do not act with these reagents, it was thought that possibly the diacetate of tribromresorcine might be better to work with than either of the ethers or the free phenol, because it holds an intermediate place between the acid tribromresorcine and its neutral ethers. Instead of using Claassen's method[1] of boiling pentabromresorcine with acetic anhydride, then with glacial acetic acid, and finally with water, the tribromresorcine diacetate was directly prepared from tribromresorcine by treating it in a sealed tube for four or five hours at 100° with either acetyl chloride or acetic anhydride, preferably the former. It is best to use a slight excess of acetyl chloride, and after the heating is finished to decompose the excess by means of water. The diacetate is easily recrystallized from alcohol and was identified by its melting-point, 108°.

After boiling tribromresorcine diacetate with water for twenty-four hours, the water was slightly pink in color, and gave a feeble test for bromides with argentic nitrate. This is due, no doubt, to the fact that water at 100° saponifies a small part of the diacetate, yielding tribromresorcine, which in its turn is acted upon by the boiling water, as before noted. In the hope of avoiding this saponification, a sealed tube containing the diacetate was heated over night at 157° with ordinary acetic acid, but the saponification was not prevented, for the result was the same as if the free tribromresorcine had been heated with water alone to that temperature. Sodic ethylate in alcoholic solution when warmed with tribromresorcine diacetate deposited a precipitate which when filtered off soon turned black. This body was undoubtedly the decomposition-product of the sodium salt of tribromresorcine. On account of the readiness, therefore, with which the diacetate was saponified, it was not worth while to carry on this line of investigation further.

[1] Ber. d. chem. Ges., 11, 1439.

Tribromnitroresorcine Diacetate, $C_6(NO_2)Br_2(OC_2H_3O)_2$.

The diacetate of tribromresorcine when added to an excess of fuming nitric acid immediately dissolved, and after standing several minutes the solution became very warm and began to boil, the body in solution becoming completely oxidized; but if just before the oxidation took place, when the solution was already hot, it was poured into an excsss of water, the resulting yellowish oil soon solidified. The substance was purified by crystallization from alcohol until it showed the constant melting-point of 161°, when it was dried at 100° and analyzed with the following results:—

0.1752 gram of the substance gave, by the method of Carius, 0.2086 gram of argentic bromide.

	Calculated for $C_6NO_2Br_2(OC_2H_3O)_2$.	Found
Bromine	50.42	50.69

The diacetate therefore behaves toward nitric acid like the tribromether rather than like the tribromphenol itself, for in the latter and in the dibromether atoms of bromine are replaced by nitro groups, as already described earlier in this paper.

Properties.—The tribromnitroresorcine diacetate forms good-sized prisms terminated by two planes at an obtuse angle to each other; it is very pale yellow, almost white, and melts at 161°. It dissolves slowly in ligroin, is readily soluble in chloroform, benzol, and ether, freely soluble in acetone, and tolerably soluble in carbonic disulphide.

In order to establish if possible the position of the three bromine atoms in tribromresorcine, attempts were made to saponify the tribromresorcinediethylether, which has the three bromine atoms arranged symmetrically. When saponified in a sealed tube with aqueous hydrochloric acid, however, the product was a red body similar to that formed by the action of water on tribromresorcine. Accordingly, in hopes of a better result, dry hydrochloric acid gas was passed for one hour over tribromresorcinediethylether heated in an oil-bath to 200°, but no saponification took place.

XCI.—TRINITROPHENYLMALONIC ESTER.[1]

By C. Loring Jackson and C. A. Soch.

At the end of his paper on the action of sodium acetacetic ester on picrylchloride, Dittrich[2] states that, in spite of many and varied attempts, he had not succeeded in making a picrylmalonic ester from picrylchloride and sodium malonic ester, but that he obtained in every case sodic picrate and viscous products of the decomposition of the malonic ester. This statement impressed us as a strange one, since in work[3] done in this laboratory it had been found that tribromdinitrobenzol acted much more easily with sodium malonic ester than with sodium acetacetic ester; for whereas a good yield of the substituted malonic ester could be obtained even when the reaction took place in the cold, with the acetacetic ester the yield was small even after the reagents had been boiled together. Accordingly we took up the study of this subject, and found, as we had expected, that the picrylmalonic ester could be obtained without difficulty. It is a white substance melting at 58°, and forms a blood-red sodium salt, which is tolerably stable, dissolving in water without decomposition. The picrylbrommalonic ester, $C_6H_2(NO_2)_3CBr(COOC_2H_5)_2$, was made by treating the substituted malonic ester with an excess of bromine; it melts at 85–86°. One object in undertaking this work was to see whether any trinitrobenzol was formed in the action of sodium malonic ester or sodium acetacetic ester on picrylchloride by the replacement of the atom of chlorine by hydrogen after the analogy of such reductions, which have been noticed frequently in the work done in this laboratory upon tribromdinitrobenzol and tribromtrinitrobenzol. Unfortunately the research was begun so late in the year that we have been unable to arrive at a definite conclusion on this subject, and it is hoped that it will be possible to repeat the experiments on a larger scale and with conclusive results early in the coming term. A bromdinitrophenylbrommalonic ester corresponding to the picryl compound mentioned above was also prepared. It melts at 72–73°.

[1] Presented to the American Academy of Arts and Sciences, May 9, 1894.

[2] Ber. d. chem. Ges., 23, 2720. [3] This Journal, 11, 93; and 12, 164.

Trinitrophenylmalonic Ester (*Picrylmalonic Ester*), $C_6H_2(NO_2)_3CH(COOC_2H_5)_2$.

As Dittrich[1] states that the product of the reaction of picrylchloride and sodium malonic ester is viscous, we first turned our attention to the preparation of the sodium salt of the substituted malonic ester in the hope that this might be purified more easily than the free ester.

Sodium Picrymalonic Ester, $C_6H_2(NO_2)_3CNa(COOC_2H_5)_2$.

The picrylchloride used in making this substance was prepared according to the method of Clemm,[2] except that we crystallized the chloride from a mixture of chloroform and alcohol, as we found that the addition of the chloroform made it possible to work with much smaller volumes of the solvent, and also seemed to prevent in great measure the deposition of the picrylchloride in an oily form. A strong cold benzol solution of 10 grams of this picrylchloride was mixed with an alcoholic solution of sodium malonic ester made from 14 grams of malonic ester and the sodic ethylate from 2.1 grams of metallic sodium. The mixture, which took on at once a deep red color, was cooled at first, and then allowed to stand for twelve hours at ordinary temperatures; after which it was diluted with about three-quarters of a liter of water. In this way a red aqueous solution was obtained, and a supernatant layer of benzol which contained a portion of the picrylmalonic ester formed, while the rest was dissolved as a sodium salt in the red aqueous solution, in addition to some sodic picrate and the sodic chloride. Upon acidifying the aqueous liquid with sulphuric acid a yellow precipitate was thrown down, which, as it settled from the liquid, collected in an oily state on the bottom of the beaker. To the oily product a strong solution of sodic hydrate was added, which imparted to it a dark red color, and after thorough mixing converted it into a red crystalline solid. To remove any liquid or viscous impurities from the salt, it was next dissolved in the smallest possible amount of alcohol and treated with an excess of benzol, after which the mixed solutions were evaporated cautiously on the steam-bath until crystals began to form, when upon cooling

[1] Ber. d. chem. Ges., **23**, 2720. [2] J. prakt. Chem. [2], **1**, 145.

the sodium salt was obtained in fine red crystals; these were washed with benzol, and after drying in a desiccator gave the following results on analysis:

I. 0.2400 gram of the substance after evaporation with sulphuric acid gave 0.0427 gram of sodic sulphate.

II. 0.8331 gram of the substance gave 0.1429 gram of sodic sulphate.

	Calculated for $C_6H_2(NO_2)_3CNa(COOC_2H_5)_2$.	Found. I.	II.
Sodium	5.85	5.76	5.56

An additional quantity of the salt was obtained by the treatment just described from the residue left after evaporating off the benzol from the solution of picrylmalonic ester in this solvent obtained by adding water to the product of the reaction.

Properties of the Sodium Salt of Picrylmalonic Ester.—It crystallizes from a mixture of alcohol and benzol in dark red crystals often a centimeter long. It is easily soluble in alcohol or ether; somewhat less soluble in water than in alcohol; nearly insoluble in benzol. It does not seem to be decomposed by any of these solvents. Strong sulphuric acid decomposes it, but without any explosion, which surprised us, as it showed a tendency to explode when dry even at comparatively low temperatures.

As the potassium salt of picric acid is so much less soluble than the sodium salt, we prepared the potassium salt of the picrylmalonic ester by treating the free ester with potassic hydrate in strong aqueous solution: but, although this salt was somewhat less soluble in both water and alcohol than the sodium salt, the difference was not very marked, and there would be no advantage in using the potassium salt instead of the sodium salt in the purification of the substance.

The behavior of an aqueous solution of the sodium salt of picrylmalonic ester with various reagents was also studied, and the following more or less characteristic precipitates were obtained:

Salt of magnesium, heavy reddish flocks.

Salts of calcium or barium, granular or crystalline precipitates of an amethyst color.

Salt of manganese, dirty yellow flocks.
Salt of nickel, light red flocks.
Salts of lead or silver, dark red flocks.
Salt of cadmium, reddish yellow flocks.

Picrylmalonic Ester, $C_6H_2(NO_2)_3CH(COOC_2H_5)_2$.

Although in our earlier experiments we prepared this substance through its sodium salt on account of the discouraging statements of Dittrich, we soon found that this was unnecessary, as the substance could be purified directly without difficulty, and in all our later work we have adopted this direct method, which we are about to describe, as it is much more convenient than the method of purification by means of the sodium salt. To prepare the picrylmalonic ester we proceeded according to the method described under sodium picrylmalonic ester, until by the addition of water the product had been divided into an aqueous and a benzol solution. The aqueous solution after acidification with dilute sulphuric acid was allowed to stand until the oily precipitate had separated completely from the mass of the liquid; part of it settled, part floated on the surface, and even during this comparatively short standing the floating part was converted into crystals; which could be used to promote the crystallization of the larger quantity on the bottom of the beaker. The solidification of the main portion of the oily product was effected without difficulty by cooling with running water, one of the crystals from the surface of the water being added if necessary; and the solidified product, after washing with cold water, was crystallized from alcohol. The benzol solution, which had been separated from the aqueous solution, was acidified with dilute sulphuric acid, and allowed to evaporate spontaneously, when it furnished a rather large additional quantity of the oily product, which, however, did not solidify so easily as that obtained from the aqueous portion, since it was necessary to allow it to stand for three or four days with occasional stirring in order to bring it into a crystalline condition. It was then pressed between layers of filter-paper, which removed an oily impurity, after which it was mixed with the crystals obtained from the aqueous liquid, and the

whole purified by crystallization from alcohol until it showed the constant melting-point 58°, when it was dried in a desiccator, and analyzed with the following results:

I. 0.2707 gram of the substance gave 28.6 cc. of nitrogen at a temperature of 25° and a pressure of 757.4 mm.

II. 0.2565 gram gave 25.9 cc. of nitrogen at a temperature of 22° and a pressure of 755.8 mm.

	Calculated for $C_6H_3(NO_2)_3CH(COOC_2H_5)_2$.	Found. I.	II.
Nitrogen	11.32	11.75	11.38

It is worthy of remark that, whereas Dittrich from the action of the picrylchloride on sodium acetacetic ester obtained a considerable quantity of dipicrylacetacetic ester, our principal product was the monopicrylmalonic ester, and only on one occasion have we observed a trace of a substance with a much higher melting-point, which we took to be the dipicryl compound. We should add that, in applying the same method to the action of sodium acetacetic ester on picrylchloride, we obtained almost exclusively monopicrylacetacetic ester.

Properties of Picrylmalonic Ester.—It crystallizes from alcohol in white, long, rather slender rectangular plates, which develop into somewhat thick prisms with blunt ends often as much as two centimeters long. It melts at 58°, and is very soluble in chloroform, ether, benzol, or glacial acetic acid; somewhat less soluble in carbonic disulphide; soluble in cold alcohol, freely in hot; rather more soluble in methyl than in ethyl alcohol; insoluble in ligroïn or cold water, slightly soluble in hot water. All the solutions of this substance except that in glacial acetic acid have a pink color, which is the more marked the stronger the solution, and the alcoholic solution imparts to the fingers a crimson color not unlike rosaniline, although less purple. This coloration of the fingers is much deeper than the color of the solution, and is tolerably fast. The formation of these pink or crimson colors from the white crystals is striking, and will be more carefully studied.

Cold strong sulphuric acid dissolves it; if this solution is warmed it turns red, and gives off bubbles of gas; dilution of the red solution after it had cooled precipitated a yellow solid.

Strong nitric acid acted in the same way, except that the picrylmalonic ester dissolves more slowly in cold nitric acid than in sulphuric acid. Strong hydrochloric acid did not dissolve it in the cold, but on warming the substance melted, and then went into solution very slowly. The picrylmalonic ester has well marked acid properties forming the red sodium salt when treated with an aqueous solution of sodic hydrate. As is often the case with substances of this class, the sodium salt is nearly insoluble in a strong solution of sodic hydrate. The sodium salt is also formed by the action of a solution of sodic carbonate on the free ester.

Trinitrophenylbrommalonic Ester (*Picrylbrommalonic Ester*),

$$C_6H_2(NO_2)_3CBr(COOC_2H_5)_2.$$

This substance was made by dissolving some of the trinitrophenylmalonic ester described in the preceding section in a small quantity of glacial acetic acid, and adding liquid bromine until it was present in distinct excess, as shown by the reddish brown color of the liquid. To make certain that the reaction was complete, the liquid was warmed gently on the steam-bath for a few minutes, and then allowed to stand at ordinary temperatures for an hour, after which water was added in excess, giving a pale yellow precipitate partly solid and partly liquid. After this had settled, the supernatant liquid, colored red with the excess of bromine, was poured off, and the liquid part solidified by cooling. It was then washed with water, dried by pressure on filter-paper, and purified by recrystallization from alcohol until it showed the constant melting-point 85°–86°, when it was dried in a desiccator, and analyzed with the following result:

0.1873 gram of the substance gave by the method of Carius 0.0789 gram of argentic bromide.

	Calculated for $C_6H_2(NO_2)_3CBr(COOC_2H_5)_2$.	Found.
Bromine	17.78	17.93

It is obvious that this atom of bromine, the presence of which is shown by the analysis, may have entered the molecule in one of two different places, either replacing the hydrogen of the malonic ester radical, as in the formula given above, or replacing one of the atoms of hydrogen attached to

the benzol ring. It is easy to determine which position the bromine occupies, for, if it is attached to the malonic ester radical, the substance will have lost all its acid properties, since the acid hydrogen has been replaced by the atom of bromine. In the second case, where the bromine is attached to the benzol ring, on the other hand, the acid properties will not be interfered with, but on the contrary will be somewhat increased if the bromine atom has any effect whatever. Upon treating our new substance with a solution of sodic carbonate no change was observed, whereas the picrylmalonic ester is converted at once into its red salt by this reagent; as therefore, this substance has no acid properties, it follows that the bromine has entered the malonic ester radical, and the formula given above is the correct one.

Properties of Picrylbrommalonic Ester.—It crystallizes from alcohol in white plates, nearly but not quite square, and much striated; these plates are arranged in irregular rather long rosettes. Less commonly it occurs in bladed or pennate forms. In general appearance it resembles acetanilide. It melts at 85°–86°; and is very soluble in chloroform or benzol; rather less soluble in ether, carbonic disulphide, or glacial acetic acid; soluble in cold alcohol, freely soluble in hot; rather more soluble in methyl than in ethyl alcohol; insoluble in cold ligroin, soluble in it when hot although with some difficulty; essentially insoluble in water, whether hot or cold. The best solvent for it is alcohol. Its alcoholic solution shows a faint pink color, similar to that given by picrylmalonic ester, but less marked. Strong sulphuric acid dissolves it in the cold with a yellow color; upon warming this solution it becomes brownish black, and bubbles of gas are given off. Strong hydrochloric acid seems to have no action on it even when hot. In cold strong nitric acid it is insoluble, but, it dissolves easily if the acid is hot, and boiling this solution for a short time produces no signs of decomposition. A strong solution of sodic hydrate did not act upon it in the cold, but, when heated with it, gave a red solution. The solution here was undoubtedly preceded by removal of the bromine. As has been stated already, sodic carbonate does not act on this substance.

Bromdinitrophenylbrommalonic Ester.

$C_6H_2Br(NO_2)_2CBr(COOC_2H_5)_2$.

This substance was made by dissolving the bromdinitrophenylmalonic ester in glacial acetic acid and adding to the strong solution an excess of liquid bromine. The bromdinitrophenylmalonic ester was made from tribromdinitrobenzol melting at 192° and sodium malonic ester.[1] After an excess of bromine had been added, as shown by the color, the liquid was warmed gently on the water-bath for a short time, and, if the color had disappeared, more bromine added. It was then, after it was cool, precipitated with water, and the substance obtained solidified by cooling, if necessary; after which it was purified by crystallization from alcohol, until it showed the constant melting-point 72°–73°. It is not wise, however, to rely on the melting-point as the only proof of purity, since the bromdinitrophenylmalonic ester from which it is formed melts at 75°–76°; we have therefore always tested our product also with a solution of sodic hydrate, which gives a red salt with the mother-substance, but has no effect in the cold on the desired compound. After purification it was dried in a desiccator, and analyzed with the following results:

I. 0.3196 gram of the substance gave by the method of Carius 0.2451 gram of argentic bromide.

II. 0.1997 gram of the substance gave 0.1550 gram of argentic bromide.

	Calculated for $C_6H_2Br(NO_2)_2CBr(COOC_2H_5)_2$.	Found. I.	II.
Bromine	33.05	32.64	33.02

The fact that this substance is not acted on by cold sodic hydrate proves that it contains the second atom of bromine attached to the malonic ester radical and not to the benzol ring.

Properties of Bromdinitrophenylbrommalonic Ester.—It crystallizes from alcohol in long white prisms terminated by a single plane at an acute angle and arranged in radiated groups;

[1] This JOURNAL, II, 93.

these crystals are sometimes a centimeter long. It melts at 72°–73°; and is very soluble in benzol, chloroform, acetone, carbonic disulphide, or glacial acetic acid; not freely soluble in cold alcohol, but easily in hot; more soluble in methyl than in ethyl alcohol, insoluble in cold ligroin, slightly soluble in hot; insoluble in water, but if boiled with water for some time, fresh water being added to take the place of that which evaporates, it is finally brought completely into solution. This action is undoubtedly due to the removal of the side-chain bromine as hydrobromic acid. It will be studied more carefully hereafter. Strong sulphuric acid does not act upon it in the cold, and when hot it acts only very slowly. Strong nitric acid also has no action when cold, but if hot dissolves it. Strong hydrochloric acid does not act upon it in the cold, and when hot has rather less effect than sulphuric acid. Strong solutions of sodic hydrate and ammonic hydrate have little or no action in the cold; when warmed they convert it into a red substance, probably a salt formed after the removal of the side-chain atom of bromine. The whole subject of the replacement of this second atom of bromine by other radicals must be studied more carefully before any account can be given of it. It is hoped that this work can be carried on in this laboratory during the coming term.

Contributions from the Chemical Laboratory of Case School of Applied Science.

XXI.—THE ARTIFICIAL PRODUCTION OF ASPHALT FROM PETROLEUM.[1]

By Charles F. Mabery and J. H. Byerley.

In the method universally employed for the separation of commercial products from petroleum, as is well known, the final product of the continuous distillation is a porous coke, and the quantity formed ordinarily is approximately equivalent to ten per cent. of the crude oil. This coke still contains a considerable proportion of hydrocarbons, but it is essentially the ultimate product of decompositions that must begin in the early stages of the distillation. The precise temperature at

[1] The results described in this paper formed the subject of a thesis by Mr. Byerley for the degree of Bachelor of Sciences.

which decomposition begins is quite variable in petroleums from different sources, and it doubtless depends somewhat on the form of the still and the manner of conducting the distillation.

In the early history of the refining of petroleum, it was accidentally discovered that distillation could be carried to a certain point with a gradual increase in the specific gravity of the distillates, when suddenly a lighter oil would appear in considerable quantities evidently formed by the decomposition of higher constituents. Since that discovery "cracking" has been practiced to increase the yield of burning-oil. The precise nature of these decompositions is not well understood.

In studying the action of heat on paraffin, Thorpe and Young[1] found that the products of decomposition included members of the series C_nH_{2n+2} and C_nH_{2n}. Of the first series nearly all the bodies then known up to $C_{10}H_{22}$ were found, and higher members which were not identified. The effect of heat on normal and isohexane and on normal pentane was thoroughly studied by Norton and Andrews.[2] Below 600° no change was observed, but between 600° and 700° decomposition began with the formation of the lower hydrocarbons C_nH_{2n+2} and C_nH_{2n}. Our results indicate that cracking begins in the vicinity of 250°, but further study is necessary concerning the action of heat on the individual higher members. An attempt will be made to determine with greater precision the nature of these decompositions. In ordinary cracking it is evident that the chemical changes may include the reaction upon one another of the various constituents of the crude oil as well as decomposition of the principal hydrocarbons.

It is a general belief that cracking consists in the breaking down of the higher constituents into lower saturated and unsaturated hydrocarbons. Determination of bromine absorption in distillates indicates an unsaturated condition, but a similar condition is likewise shown by the quantity of bromine absorbed in the crude oils, only in a less degree than in the higher distillates. Without doubt the point at which cracking begins is quite variable in oils from different sources.

[1] Ann. Chem. (Liebig), 165, 1. [2] This JOURNAL, 8, 1.

Indeed it is not difficult to demonstrate the difference in oils from the same source, but from different levels in the same well. In an examination of Berea Grit petroleum by O. C. Dunn and one of us (C. F. M.), which will be described in another paper, distillates were prepared in which bromine absorption was determined for this paper, showing a marked variation in the quantity of bromine absorbed in the oils from different depths.

	1.		2.		3.	
	A.	B.	A.	B.	A.	B.
Crude	7.62	3.00	8.28	2.35	9.49	2.64
35–60°	0.00	0.00	0.00	0.00	0.79	0.51
60–85°	0.00	0.00	0.00	0.00	1.19	0.90
85–110°	0.74	0.20	1.50	0.75	1.82	0.87
110–135°	1.81	0.65	3.03	1.17	2.32	0.77
135–160°	2.32	1.61	3.52	1.39	3.71	0.95
160–185°	2.24	1.36	3.79	1.37	4.94	1.25
185–210°	2.32	0.94	5.20	1.13	5.94	1.83
210–235°	2.08	0.51	5.75	1.93	6.66	2.37
235–260°	3.87	0.52	8.09	2.49	7.76	2.06
260–285°	4.84	1.12	8.66	2.24	9.18	2.58
285–310°	5.69	1.93	9.42	2.76	11.03	3.04
310–335°	4.58	2.01	11.70	3.97	10.98	3.74
335–360°	7.57	2.33	17.01	5.63	24.84	4.53
+360°	9.72	1.12	18.54	6.07	26.38	9.08

	4.		5.		6.	
	A.	B.	A.	B.	A.	B.
Crude	5.93	1.41	9.96	3.47	6.26	2.23
35–60°	0.00	0.00	0.26	0.27	0.00	0.00
60–85°	1.73	1.73	0.54	1.08	0.00	0.00
85–110°	2.92	2.22	1.38	1.66	0.00	0.00
110–135°	3.65	3.36	2.76	1.81	1.56	0.42
135–160°	4.04	1.46	3.75	1.74	1.63	1.54
160–185°	5.03	1.41	5.14	1.48	2.46	1.58
185–210°	5.64	2.08	5.41	2.00	3.54	1.94
210–235°	6.26	2.16	8.00	2.60	4.32	2.41
235–260°	8.54	2.22	8.01	2.27	6.31	2.94
260–285°	10.21	3.15	9.29	2.48	7.58	3.07
285–310°	9.38	2.43	10.47	4.49	9.60	2.83
310–335°	11.24	2.36	10.82	3.09	9.09	3.59
335–360°	18.01	3.23	17.60	6.01	13.59	3.56
+360°	21.84	3.84	20.31	7.08	16.89	5.01

In column A are given the percentages of bromine absorbed, and in column B the percentages of hydrobromic acid set free. Oil No. 1 was taken from the 140 foot sand, Macksburg; oil No.

2 from the 300 foot sand; oil No. 3 from the 500 foot sand; oil No. 4 from the 700 foot sand; oil No. 5 from the 1500 foot sand; and oil No. 6 from the 1500 foot sand, Archer's Fork, Ohio.

It is evident that the hydrobromic acid evolved follows with some regularity the absorption of bromine, increasing with the temperature of distillation. The larger quantity of acid formed in the higher distillates is doubtless due, at least in part, to the presence of normal constituents of the crude oil, since the latter evolves considerable hydrobromic acid.

To ascertain the influence of still higher temperatures, a residue + 360° in an oil taken from a well in the Berea Grit, 1500 foot level at Archer's Fork, Ohio, (I), and a similar residue from Lima oil (II) were further distilled with a 550° thermometer and collected within limits of 25°. The specimen of Lima oil apparently cokes less readily than the other, and its bromine absorption shows less variation.

	300–325°	322–350°	350–375°	375–400°	400–415°	
I.	14.71	24.70	31.22	19.83	Coke	....
II.	....	27.19	19.04	26.98	31.26	Coke

Attention has been called[1] by one of us (C. F. M.) to the necessity of excluding air during distillation at high temperatures to avoid decomposition. In further evidence as to the influence of air, we submitted two portions of Berea Grit oil, 1500 foot level to distillation, one portion (I) under ordinary conditions, and a second portion (II) with a current of air passing through the oil during distillation. The decomposition produced by the action of air on the hot oil is shown by the increase in bromine absorption A, in all distillates. The values in columns B represent the weight of hydrobromic acid evolved from the total weights of the respective fractions. Beyond showing comparative qualities, the latter observations are not of especial importance.

[1] Proc. Amer. Acad., **31**, 8.

	I.		II.	
	A.	B.	A.	B.
–100°	0.00	0.00	0.00	0.00
100–125°	0.42	0.19	0.49	0.21
125–150°	0.97	0.42	1.74	0.28
150–175°	2.26	1.34	6.11	1.88
175–200°	2.31	0.41	8.15	3.92
200–225°	3.90	1.31	11.66	3.53
225–250°	7.66	2.18	13.48	1.35
250–275°	9.76	1.07	14.28	8.25
275–300°	9.62	3.22	16.36	1.72
300–325°	14.71	2.79	15.54	5.81
325–350°	17.34	18.51	22.51	11.83
350–375°	31.22	20.15	38.64	15.83
375–400°	....	....	49.48	18.86

It has long been felt that products should be obtained from the less volatile portions of petroleum with a greater value than the coke which is the final product in the ordinary process of refining. Many attempts have, therefore, been made to conduct the final distillation in such a manner that the heavier portions may be protected from decomposition and converted into a form suitable for the preparation of asphalt or similar products.

Mr. F. X. Byerley was the first to discover the conditions necessary to prevent ultimate decomposition, and he has perfected a method which renders possible the separation of commercial products that are serviceable in the manufacture of the various grades of asphalt, such as are used in varnishes, roofing and paving. This method has been protected by letters patent, and, under the control of a large corporation, the manufacture of these materials will doubtless assume large proportions.

As shown by our own experiments described above, although the introduction of air during distillation produces greater decomposition, the first series of distillates collected under ordinary conditions, give evidence of considerable change, especially in the higher fractions. In the Byerley method these changes are prevented to a large extent by very slow distillation. The material employed in the preparation of asphaltic products by this method is the heavy residual oil with a specific gravity between 25° and 28° Baumè that re-

mains after distillation of the portion used in the preparaiion of burning oil. A determination of the specific gravity of one specimen of this tar at 20° gave 0.9325. It absorbed 12.18 per cent. of bromine, and gave off 2.23 per cent. of hydrobromic acid.

This tar is subjected to distillation in stills of the "cheese box" type with steel bottoms, enclosed in a brick chamber. These stills are somewhat less in diameter than in height, and the capacity of each is 150 barrels. For the introduction of air every still is supplied with five vertical iron pipes, each one and one-half inches in diameter, extending to within a few inches of the bottom of the still. A six-inch pipe leads from the top of the still to condensers, and these are attached to a closed iron chamber, to which is connected the air-pump for exhaustion. Ordinarily a suction equivalent to five or six inches of water in excess of that required to overcome the column of oil, is sufficient for continuous operation. The stills are filled about one-half with tar, and heat is applied solely to the bottom. The temperature is controlled by means of a pyrometer inserted into the tar. At first it is raised to 450° and later to 650° F., where it is maintained during the distillation. Much depends upon the rate of distillation, since, if it proceeds too rapidly, the yield is small, and the product inferior. The quantity of the distillate affords an easy means of control. The distillate has the properties of the less volatile portions of burning oil; it is dark red in color, but it can be nearly bleached by refining with sulphuric acid. It begins to distil at about 320°, and its specific gravity at 20° varies between 0.8393 in the first distillate and 0.8584 in the later portions. A specimen of the first distillate contained 0.15 per cent. of sulphur, and it absorbed 10.66 per cent. of bromine; the second gave 0.04 per cent. of sulphur, and it absorbed 16.27 per cent. of bromine. After treatment with steam, sulphur was completely removed from the first distillate. In practice one separation is made of the distillates, and both are refined for burning oils. The grade of product depends upon the duration of the distillation which is ordinarily completed in four or five days. The farther it is carried the more solid is the asphalt.

The air doubtless serves several purposes. It causes oxidation to a certain extent, especially if the tar is a residue from a sulphur oil. As shown by analysis, the asphalts contain a small proportion of oxygen, although not much in excess of what should be derived from the crude oil, assuming, which is probable, that the larger portion of the oxygen compounds do not distil with the burning-oil distillates. Then the tar is protected during distillation from the decomposing action of the hot still bottom by the currents of air which keep it constantly in motion. The volatile constituents suffer less decomposition, except from the oxidation of sulphur, than the distillates in the ordinary process of cracking.

Some water is evolved as an oxidation-product, and much sulphur appears in the form of sulphurous and sulphuric acids. A considerable proportion of the sulphur remains still unoxidized in the asphalts and less in the oily distillate. The commercial products include (1) liquid asphalt, (2) roofing asphalt, (3) paving asphalt, (4) Byerlyte or varnish asphalt.

The liquid asphalt (1) is used as a flux for natural asphaltum in the preparation of paving and roofing asphalts. It begins to flow at 25°. Its composition was determined by analysis:

Carbon	86.22
Hydrogen	10.91
Sulphur	0.30
Nitrogen	0.18
Oxygen, by difference	2.39
Specific gravity at 20°	0.9560
Bromine-absorption	14.18
HBr evolved	2.23

The product (2) used in the manufacture of roofing, tar-paper, and in the construction of telephone conduits and insulators was examined as to its chemical and physical properties with the following results:

Carbon	86.48 per cent.
Hydrogen	10.33 "
Sulphur	0.40 "
Nitrogen	0.61 "
Oxygen, by difference	2.18 "
Specific gravity at 20°	1.00 "
Bromine-absorption	14.93 "
HBr evolved	2.91 "

Softening and melting-points:

20°	105°	135°
Easily compressible in fingers.	Shape still retained.	Begins to flow.

The next higher grade (3) that is adapted for paving does not differ essentially in its composition from the preceding; it flows at a higher temperature:

Carbon	86.90
Hydrogen	10.20
Sulphur	0.39
Nitrogen	0.63
Oxygen	1.88
Specific gravity	....
Bromine-absorption	14.40
HBr evolved	1.64

Softening and melting-points:

20°	135°	150°	165°
Slightly compressible in fingers.	Retains shape; edges rounded.	Softens.	Begins to flow.

To the grade next higher (4) has been given the name Byerlyte from the inventor of the process. It resembles the natural product Gilsonite, in that it is an excellent material for the manufacture of the best grades of japans and black varnish. Its composition was also determined by analysis:

Carbon	87.44
Hydrogen	9.31
Sulphur	0.41
Nitrogen	0.64
Oxygen	2.20
Specific gravity	1.04
Bromine-absorption	18.93
HBr evolved	4.56

Softening and melting-points:

20°	160°	230°	260°
Not compressible by fingers.	Slightly rounded on edges.	Softens.	Begins to flow.

In testing the solubility of Byerlyte, it was evident that it contains no fixed carbon. It dissolves completely in carbonic disulphide. In light ligroïn, 75–110°, 62.45 per cent. is solu-

ble and 37.55 per cent. insoluble. In petroleum distillate, 200–250°, 59.37 per cent. is soluble, 40.03 per cent. insoluble.

It therefore appears that ultimate decomposition of petroleum tar is entirely prevented by this method of distillation. The influence of air in oxidation evidently affects the removal of hydrogen, as shown by the diminished proportions of this element, and the appearance of water in the process of manufacture, rather than the formation of oxygen compounds in the oil.

As explained above, the product Byerlyte has been found to possess properties desirable in the manufacture of varnishes. It resembles closely in its physical properties and its chemical composition the natural bitumen found in Colorado and Utah, and known in commerce as Gilsonite. This substance is used in large quantities by the manufacturers of varnish. In an analysis of Gilsonite from the Wasatch range in Eastern Utah, we obtained the following results:

		1.	2.	3.
C	86.86			
H	11.89			
N	0.02			
S (by Carius)		0.60		
(by combustion)			0.64	0.68

In an investigation of Utah Gilsonite recently made by Dr. W. C. Day,[1] it was found that this substance like Byerlyte is entirely soluble in carbonic disulphide, but less soluble in petroleum ether than we found Byerlyte to be. As shown by the determinations of sulphur given above, our experience concerning such determinations by combustion and by the Carius method does not coincide with that of Dr. Day. In the adaptation of the Sauer-Mixter-Burton method, perfected by one of us,[2] for the determination of sulphur in volatile organic compounds it was not explained that this method is serviceable in the analysis of non-volatile substances, or, what is doubtless true, that it is applicable to any compounds that can be burned with the formation of volatile products. Gilsonite is somewhat irregular in volatilizing, but not more so than the higher organic sulphides, several of which have

[1] Journal of the Franklin Institute, June, 1895.

[2] Mabery: Proc. Am. Acad., 30, 1; This JOURNAL, 16, 544.

been analyzed in this manner. With adherence to the precautions given in the paper cited above, the combustion can be easily controlled. The same is true in the application of the Carius method to the analysis of Gilsonite. Following the details outlined in the same paper, no difficulty whatever was found in reaching accurate results.[1] Nitrogen was determined by the Kjeldahl method which we have found to be convenient and accurate in the analysis of petroleum and allied products. The marked differences in the percentages of carbon, hydrogen, and sulphur which we obtained, and those given by Day indicate a considerable variation in the composition of Gilsonite.

ON THE ACTION OF PHOSPHORUS PENTACHLORIDE ON PARASULPHAMINEBENZOIC ACID.

By Ira Remsen, R. N. Hartman, and A. M. Muckenfuss.

Some years ago one of us (I. R.) with Dohme[2] showed that when benzoic sulphinide is treated with phosphorus pentachloride at a somewhat elevated temperature, the principal product of the reaction is orthochlorcyanbenzene, $C_6H_4<^{Cl}_{CN}$. A little later Rich,[3] at the suggestion of one of

[2] This Journal, 11, 347. [3] *Ibid.*, p. 348.

[1] There is another feature in the determination of sulphur by combustion that perhaps should be mentioned in this connection. In burning substances with small percentages of sulphur we have found no difficulty in securing accurate results as shown by parallel Carius determinations. Occasionally, compounds with higher percentages of sulphur have given too low results, although usually they have been satisfactory. It has been shown by Lunge and others that methyl orange is not sensitive to neutral sodic sulphite, but the end reaction is determined by the acid sulphite.

These results have been confirmed in this laboratory by Prof. A. W. Smith in a series of carefully conducted determinations. It is therefore evident that, in substances with low percentages of sulphur, the oxidation is complete with the formation only of sulphuric acid. With high percentages, some of the sulphur may be absorbed as sulphurous acid, although the quantity of this acid is never large. This error may be avoided by the addition of hydrogen dioxide in small amount, which oxidizes any sulphurous acid, and the titration is then only concerned with sulphuric acid.

The objection that has been suggested to the Carius method, that is the small amount of substance, 0.2000–0.3000 gram conveniently oxidized in a closed tube, is not valid, since results by this method agree closely within a few thousandths of one per cent. in low sulphur oils, with values obtained by combustion in air, even when as much as 3.000 grams of oil are completely burned, as we have recently found. In recent experiments, it has been shown that the correct percentage of sulphur can be ascertained only by combustion of the entire quantity of oil weighed. We are

us (I. R.), took up the study of the action of phosphorus pentachloride on parasulphaminebenzoic acid. He obtained parachlorcyanbenzene, which he studied to some extent, but the investigation was interrupted, and various circumstances have interfered with its further prosecution until recently. The results of the later investigation are recorded in the following paper. As will be seen, when phosphorus pentachloride acts upon parasulphaminebenzoic acid at a temperature below 70°, a product of the formula $C_6H_4<^{COCl}_{SO_2.NPCl_2}$ is formed. When this is heated to between 146° and 200°, phosphorus oxychloride is given off, and paracyanbenzenesulphone chloride, p-$C_6H_4<^{CN}_{SO_2Cl}$, is formed, thus:

$$p\text{-}C_6H_4<^{COCl}_{SO_2.NPCl_2}=p\text{-}C_6H_4<^{CN}_{SO_2Cl}+POCl_3.$$

When paracyanbenzenesulphone chloride is heated to 205°, it is decomposed, giving sulphur dioxide and parachlorcyanbenzene according to this equation:

$$p\text{-}C_6H_4<^{CN}_{SO_2Cl}=p\text{-}C_6H_4<^{CN}_{Cl}+SO_2.$$

These facts are of considerable interest, as they give some insight into the nature of the reactions that lead to the shifting of the nitrogen atom from the sulphone group to the carbon atom in the para position. In a later article it will be shown that when parasulphaminebenzoic acid is heated alone to a temperature near its melting-point, it is completely transformed into other substances, the formation of which involves a shifting of the nitrogen atom in the molecule. A similar result is reached when metasulphaminebenzoic acid is heated, and the products of this transformation are now being investigated in this laboratory by Dr. Walter Jones.

now able to state with confidence, that no method at present known for the determination of sulphur in organic bodies excels in accuracy combustion in air or oxygen. In case of execution no other method approaches it. In the form recently proposed by me, (This JOURNAL, 16, 544,) I believe it can be applied without difficulty to any organic compound composed of carbon, hydrogen, oxygen, and sulphur. Whether a large percentage of nitrogen would interfere, we have not determined, but probably it would not.

[1] Ann. Chem. (Liebig), 178, 297.

Action of Phosphorus Pentachloride at 60°. — The parasulphaminebenzoic acid used in these experiments was prepared by oxidizing either paratoluenesulphoneamide according to the method described by Remsen,[1] or from commercial saccharin, of which it forms about fifty per cent., by the method of Remsen and Burton.[2]

10 grams of the dried parasulphaminebenzoic acid and 21 grams of phosphorus pentachloride are thoroughly mixed in a dry mortar and quickly brought into a dry Erlenmeyer flask, which is then kept free from atmospheric moisture by connection with a small U-tube containing a little sulphuric acid. The flask is clamped in position in a sulphuric-acid bath, and the temperature is gradually raised. When, at about 60°, reaction sets in, the flask is raised above the bath until evolution of hydrochloric acid ceases; then it is lowered again, raised again, and so on, until action at 60° is complete. The temperature is then raised slowly to 110°, the flask being shaken from time to time, and this temperature is maintained until no more oxychloride collects in the U-tube, and the liquid in the flask is transparent. The flask is then allowed to cool slowly and about 200 cc. of dry ligroïn is added. The whole is now vigorously shaken for a few minutes. The clear, yellow oil soon solidifies to a mass of beautiful crystals, while the ligroïn, which is poured off, is found to contain phosphorus and chlorine. 500 cc. of fresh ligroïn is now poured into the flask, which is then immersed in water kept at 70°. The mass again becomes oily as the temperature rises, and is constantly stirred up into the ligroïn with a glass rod. When the ligroïn has reached 70°, it is kept there five minutes, and then filtered through a dry fluted filter. The flask is well stoppered, and allowed to stand from twelve to twenty-four hours, when it is found to contain a considerable quantity of very beautiful, transparent, stout prisms, that often attain the length of an inch.

Care must be taken to let the reaction at 60° proceed as slowly as possible, and especially not to heat the ligroïn above 70°. If the heating is carried much above this temperature, dark, oily products are formed, that become hopelessly intermingled with the clear crystals.

[1] Ann. Chem. (Liebig), 178, 297. [2] This JOURNAL, 11, 403.

The ligroïn over the crystals is well stirred and poured off. Fresh ligroïn is added several times and the lighter products thus fully poured off. The clinging crystals are then detached from the glass, and all are poured into a beaker under ligroïn, and carefully examined. Every dark piece present is withdrawn. The clear product is then thrown on a filter, washed with fresh ligroïn, quickly and well pressed out on drying paper and placed in a sulphuric-acid desiccator.

Analysis led to the empirical formula $C_7H_4NO_3SPCl_4$, which corresponds to p-$C_6H_4<\begin{matrix}COCl\\SO_2.NPCl_2\end{matrix}$

I. 0.287 gram gave 0.0408 gram H_2O, and 0.2528 gram CO_2.

II. 0.2914 gram gave 0.0385 gram H_2O, and 0.255 gram CO_2.

III. 0.4006 gram gave 15 cc. of nitrogen and 23° and 760.55 mm.

IV. 0.4128 gram gave 16.3 cc. of nitrogen at 26° and 761 mm.

V. 0.2439 gram gave 0.168 gram $BaSO_4$ (Carius).

VI. 0.4472 gram gave 0.1412 gram $Mg_2P_2O_7$.

VII. 0.3630 gram gave 0.562 gram AgCl.

VIII. 0.2887 gram gave 0.4502 gram AgCl.

	Theory.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
C	23.69	24.02	23.93	...	...	...	...	...	...
H	1.13	1.58	1.47	...	...	...	...	...	...
N	3.95	...	...	4.22	4.37	...	...	...	...
O	13.53	...	...	...	...	...	...	...	...
S	9.03	...	...	...	...	9.46	...	...	...
P	8.74	...	...	...	...	...	8.81	...	...
Cl	39.92	...	...	...	...	...	...	38.35	38.59

Chlorine was determined by placing about 0.2 gram in 400 cc. of water, warming until dissolved, and precipitating as silver chloride. Phosphorus was determined by placing about 0.2 gram in 100 cc. of water, heating to boiling, filtering off the parasulphaminebenzoic acid that separates out on cooling, and precipitating from the filtrate as ammonium magnesium phosphate.

Phosphochlorparasulphaminebenzoic Chloride.—The results

above recorded do not agree very closely with the calculated figures, because of the extreme instability of the substance. It absorbs moisture from the atmosphere with great avidity, giving off fumes of hydrochloric acid. The specimens analyzed for chlorine were made at different times, and were in both cases protected from moisture as much as possible; yet the figures are about 1½ per cent. too low, some hydrochloric acid being given off in the process of pressing dry. The loss of chlorine of course increases the percentages of the other elements. The compound has such a tendency to absorb water, give off hydrochloric acid, and become liquid, that it can not be pressed dry with filter-paper except on a dry day. The substance crystallizes beautifully from ligroïn in transparent prisms that are not truncated by any well-defined faces. When exposed to the air the crystals quickly turn white. They break down in water, dissolving quickly if the water is warm, and pure parasulphaminebenzoic acid is deposited from the solution on cooling. The phosphochloride melts at 82°. It is soluble in benzene, but no well defined crystals were obtained from the solution.

Constitution of Phosphochloroparasulphaminebenzoic Chloride.—That the compound has the constitution represented by the formula $p\text{-}C_6H_3{<}^{COCl}_{SO_2N} : PCl_2$, appears probable in view of the fact that it breaks down so easily with water forming parasulphaminebenzoic acid. The reaction is expressed by the following equation:

$$p\text{-}C_6H_4{<}^{COCl}_{SO_2N} : PCl_2 + 2H_2O = p\text{-}C_6H_4{<}^{COOH}_{SO_2NH_2} + HCl + POCl_3.$$

The phosphorus oxychloride would, of course, yield phosphoric acid by the action of the water, and the only products found were parasulphaminebenzoic, hydrochloric and phosphoric acids. Further, an analogous substance has been obtained by the action of phosphorus pentachloride on benzenesulphonamide. Wichelhaus[1] gave the formula $C_6H_4.SO_2NH.PCl_2$ to the product, but Wallach and Huth[2] later showed

[1] Ber. d. chem. Ges., 2, 502. [2] Ibid. 9, 424.

that it is to be represented by the formula $C_7H_5SO_2.NPCl_2$.

Search for Other Products.—If the mass remaining after the extraction of the phosphochloride is extracted with fresh ligroïn, each successive portion that separates on cooling contains less chlorine than the preceding one, and all pass to parasulphaminebenzoic acid on treatment with water. Thus, 38.35, 37.00, 32.89, and 30.07 per cent. of chlorine were found in the analysis of four successive extracts. The last product, containing 30.07 per cent. of chlorine, was found to be identical with that obtained by treating the phosphochloride with ligroïn at 70°, when phosphorus oxychloride was extracted. About one-fourth of the substance dissolved, and on cooling, a substance separated from the filtrate, that gave 30.14 per cent. of chlorine on analysis and was identical in appearance with that giving 30.07 per cent. It was very difficultly soluble, only about 0.2 gram separating from a liter of ligroïn, and consisted of silky hair-like crystals. It contained no phosphorus.

If the same ligroïn, containing phosphorus oxychloride and hydrochloric acid, was used for the successive extracts, a substance was finally obtained that separated in long, slender, arborescent crystals, of very beautiful appearance. These broke up completely on the slightest agitation, and could not be pressed dry for analysis.

If the ligroïn from the phosphochloride was filtered into a wet vessel, fine needles gradually separated. It was not possible to determine the composition of these products. They appeared, however, to be formed by decomposition of the phosphochloride.

Action of Heat on Phosphochlorparasulphaminebenzoic Chloride.—A quantity of the purified phosphochloride was placed at the bottom of a tube, fused at one end, and arranged to rest in a sulphuric-acid bath. Not far from the substance the tube was bent into two successive ∪-forms, the one nearest the substance being arranged to dip under water and the other being moistened with sodium hydroxide solution. Beyond this latter, the tube was drawn out to a coarse capillary about two inches long. The bath was heated slowly. The phosphochloride melted sharply at 82°, and began to give off vapors

at 146°. The temperature was gradually raised to 200°, and kept there until no more gas was evolved. The mass blackened considerably, a yellow substance in the form of clear needles sublimed just above the bath, and a liquid collected in the U-bend nearer the bath. The tube was broken at each end of this bend, and the three parts examined. The substance in the farther bend gave off sulphur dioxide on addition of sulphuric acid. The liquid in the nearer bend was transferred to cold water, when it settled to the bottom as an oil, but gradually dissolved. The solution was found to contain hydrochloric and phosphoric acids.

The tube containing the charred residue and the sublimate was broken into fragments, extracted with benzene, and the filtered extract evaporated to dryness. The residue thus obtained was placed in a distilling-bulb, water added, and half of the liquid distilled over into another vessel. The distillate contained a white substance that had a very decided odor of nitriles, was very volatile with water-vapor, and melted at 93°. These are the properties of parachlorbenzoic nitrile, as will be shown further on. The liquid remaining in the distilling-bulb was filtered, and found to contain hydrochloric acid and a non-volatile acid. It was evaporated to dryness, the solution of the residue neutralized with barium carbonate, and the filtrate from this evaporated to crystallization. Seed-like crystals appeared, which proved to be the barium salt of paracyanbenzenesulphonic acid.

It appears from these observations that among the reactions that take place when the phosphochloride is heated is that represented by this equation:

$$p\text{-}C_6H_4{<}^{COCl}_{SO_2.NPCl_2} = p\text{-}C_6H_4{<}^{CN}_{SO_2Cl} + POCl_3.$$

Action of Phosphorus Pentachloride between 150° and 200°.

Parasulphaminebenzoic acid and phosphorus pentachloride, in the proportion of two molecules of chloride to one of acid, are thoroughly mixed, and then brought into a retort of suitable size, through whose tubulure a thermometer is introduced in such a way that its bulb is covered by the mass in the retort. The retort, with its contents, is then placed in a bath,

of oil or concentrated sulphuric acid, and the temperature gradually raised. Reaction does not take place immediately, but when the mass reaches a temperature of 60° C. it begins to soften, and energetic action soon sets in, with evolution of hydrochloric acid and a considerable rise of temperature. The source of heat is removed at this stage, to moderate the reaction to some extent, as it has been found that too rapid action leads to unsatisfactory results. After the first energetic action is over, and the contents of the retort have become liquid, the temperature is raised again until the reaction continues as before, with evolution of hydrochloric acid and formation of phosphorus oxychloride. When the boiling-point of phosphorus oxychloride (110° C.) is reached, the mass is kept at this temperature until the reaction is apparently completed, and all the oxychloride has distilled off. If the temperature is raised to about 150° C., a second reaction sets in, and another portion of phosphorus oxychloride distils off. The heating is continued gradually until the thermometer dipping into the fused mass indicates a temperature of about 200° C., and the retort is kept at that point until the secondary reaction is over and no more oxychloride distils off. When this stage of the reaction is reached, the contents of the retort, which form a dark-brown semi-transparent liquid, are poured into a suitable vessel, and when cool they crystallize in well-defined prisms, rendered impure by the presence of some phosphorus compounds and a little parachlorbenzonitrile, which is formed in small quantities if the temperature rises too high. It is advisable to proceed quite slowly and not allow the contents of the retort to be heated above 220° C., as at high temperatures the product is gradually decomposed into sulphur dioxide and parachlorbenzonitrile. When the reaction is carried out as here described, a good yield of the new product is obtained. An experiment gave the following result: From 135 grams of parasulphaminebenzoic acid and 280 grams of phosphorus pentachloride, 135 grams of the new product, in approximately pure condition, was obtained. This approaches very closely to the theoretical yield. Experiments carried on with smaller quantities of material gave yields varying between 80 and 95 per cent. The

product is separated from phosphorus compounds by treating it with water and by recrystallizing it from chloroform and benzene, from which it separates in large transparent prisms. The product, purified by successive recrystallizations, was then subjected to analysis. The results lead to the empirical formula $C_7H_4O_2SNCl$.

I. 0.2336 gram substance gave 0.3615 gram CO_2, and 0.0497 gram H_2O.

II. 0.2504 gram substance gave 0.3790 gram CO_2, and 0.0530 gram H_2O.

III. 0.3217 gram substance gave 19.90 cc. nitrogen at 18° C. and 760.1 mm.

IV. 0.3528 gram substance gave 21.60 cc. nitrogen at 18° C. and 759.3 mm.

V. 0.2569 gram substance gave 0.1775 gram AgCl and 0.2990 gram $BaSO_4$.

VI. 0.1723 gram substance gave 0.2017 gram $BaSO_4$.

VII. 0.2658 gram substance gave 0.1890 gram AgCl.

	Calculated for $C_7H_4SNClO_2$.	Found. I.	II.	III.	IV.	V.	VI.	VII.
C,	41.67	41.65	41.28	...	...	...	...	...
H_4	2.00	2.33	2.35	...	...	...	...	...
N	6.96	...	...	7.13	7.05	...	...	...
S	15.60	...	...	...	...	16.00	16.90	...
Cl	17.50	...	...	...	...	17.00	...	17.58

These results considered in connection with the conduct of the substance show that it is *p*-cyanbenzenesulphone chloride, *p*-$C_6H_4{<}^{CN}_{SO_2Cl}$, and its formation must be represented by the equation:

$$C_6H_4{<}^{COOH}_{SO_2NH_2} + 2PCl_5 = C_6H_4{<}^{CN}_{SO_2Cl} + 2POCl_3 + 3HCl.$$

Paracyanbenzenesulphone chloride crystallizes beautifully from benzene, crystals several centimeters in length and a centimeter in thickness being easily obtained. They are large rhombic prisms perfectly transparent. Frequently both ends are terminated by well-developed planes. It has a faint odor resembling that of the toluenesulphone chlorides. In the air it is stable, and it is not attacked by cold water. By long boiling with water, however, it is decomposed.

Alcohol dissolves it slowly at ordinary temperatures, the corresponding acid being formed. It dissolves readily in chloroform, benzene, and glacial acetic acid. It is much less soluble in ether, and almost insoluble in ligroïn. It melts at 111–112°, and sublimes in rough, white needles. When heated to about 250°, it is gradually decomposed, giving off sulphur dioxide, and forming parachlorcyanbenzene.

When the chloride is boiled with water it is easily converted into paracyanbenzenesulphonic acid, p-$C_6H_4{<}^{CN}_{SO_3OH}$. When heated with water at 200° in a sealed tube it yields the acid ammonium salt of parasulphobenzoic acid. This was identified by transforming it into the very characteristic acid barium salt described by Remsen.[1] On analysis the salt gave the following results:

	Calculated.	Found.
Ba	23.12	23.03
H_2O	9.10	9.24

When the chloride is treated with aqueous ammonia, a well-characterized amide is formed. This, by treatment with alkalies or by heating with water in a sealed tube, is converted into parasulphaminebenzoic acid. These reactions show clearly that the chloride has the constitution above assigned to it, viz., $C_6H_4{<}^{CN}_{SO_2Cl}$.

Paracyanbenzenesulphonic Acid, $C_6H_4{<}^{CN}_{SO_3OH(p)}$.—When paracyanbenzenesulphone chloride is boiled with water it is easily converted into the corresponding acid. This substance is extremely soluble in water even in the cold, but by gradual concentration of the solution it separates in small prismatic crystals. Owing to its great solubility, it was not possible to purify it sufficiently for analysis. Several salts, however, were prepared, the analyses of which leave no doubt as to the composition of the acid.

Barium Paracyanbenzenesulphonate, $(C_7H_4SO_3N)_2Ba$.—This salt is moderately soluble in hot water, difficultly in cold, and crystallizes in spherical aggregates of seed-like crystals without water of crystallization. The analyses gave these results:

[1] Ann. Chem. (Liebig), 178, 280.

I. 0.2241 gram of salt gave 0.1032 gram $BaSO_4$.

II. 0.3408 gram of salt gave 0.1577 gram $BaSO_4$.

	Calculated for $(C_7H_4SO_3N)_2Ba$.	Found. I.	Found. II.
Ba	27.36	27.09	27.21

Potassium Paracyanbenzenesulphonate, $C_7H_4SO_3NK$.—This is very readily soluble in water, but by slow evaporation of the solution it separates in long transparent prisms, frequently an inch in length. The crystals sometimes have their planes striated longitudinally and are quite characteristic. The analysis of the dry salt gave this result:

0.2132 gram salt gave 0.081 gram K_2SO_4.

	Calculated for $C_7H_4SO_3NK$.	Found.
K	17.68	17.03

Paracyanbenzenesulphoneamide, $C_6H_4<^{CN}_{SO_2NH_2}(p)$.—This is quite readily soluble in boiling water, but difficultly in cold water; readily soluble in hot alcohol; very slightly soluble in ether. It crystallizes from water in lustrous prisms, often two inches in length. When heated with a quantity of water insufficient for complete solution, the amide melts to an oil, which solidifies to a crystalline mass on cooling. This property of fusing under water has been noticed in several of the derivatives studied. The amide melts at 168–169° C., and can be sublimed with difficulty. Heated with hydrochloric acid in a sealed tube to 200° C., it gives parasulphaminebenzoic acid. This transformation, as has been shown before, has a direct bearing on the question of the constitution of the amide, and, taken in connection with the method of preparation, shows conclusively that the formula ascribed to the compound is the correct one. The analyses gave these results:

I. 0.1062 gram substance gave 0.2080 gram $BaSO_4$.

II. 0.1849 gram substance gave 0.2369 gram $BaSO_4$.

III. 0.3540 gram substance gave 49.22 cc. nitrogen at 22° C. and 762.8 mm.

IV. 0.2842 gram substance gave 39.15 cc. nitrogen at 21° C. and 758.8 mm.

	Calculated for $C_7H_4O_4N_2S$.	Found. I.	II.	III.	IV.
S	17.60	17.83	17.61	....	....
N	15.42	....	....	15.78	15.62

Paracyanbenzenesulphoneanilide, $C_6H_4<^{CN}_{SO_2NHC_6H_5(p)}$.—This compound is formed by bringing together, best in benzene or chloroform solution, one molecule of paracyanbenzenesulphone chloride and two molecules of aniline. Reaction takes place at once with evolution of heat. The semi-liquid product is heated for some time to ensure complete reaction of the substances. The product is boiled with water and dilute hydrochloric acid, and is then purified by crystallization from alcohol, from which it separates in long prismatic plates usually with a slight brown color. When crystallized from benzene, the anilide has an entirely different crystal-habit and separates in tufts of fine, flat needles with a satiny lustre. It is readily soluble in alcohol and glacial acetic acid, less soluble in benzene, and almost insoluble in ether. It is very slightly soluble in boiling water, first melting to an oily liquid. When the aqueous solution is concentrated, the anilide separates again, giving the solution a milky appearance. Alkalies dissolve it in the cold, and from this solution it is reprecipitated by acids. The anilide fuses at 112° C. and forms a transparent mass which does not solidify again until entirely cold. The analytical results are as follows :

I. 0.3169 gram substance gave 0.2840 gram $BaSO_4$.

II. 0.2398 gram substance gave 0.2210 gram $BaSO_4$.

III. 0.3294 gram substance gave 32.50 cc. nitrogen at 21.2° C. and 753 mm.

IV. 0.3504 gram substance gave 34.20 cc. nitrogen at 10° C. and 759.5 mm.

	Calculated for $C_{13}H_{10}O_2N_2S$.	Found. I.	II.	III.	IV.
S	12.41	12.31	12.66	....	....
N	10.89	....	....	11.09	11.19

Parasulphanilidobenzoic Acid, $C_6H_4<^{COOH}_{SO_2NHC_6H_5(p)}$.—When paracyanbenzenesulphoneanilide is treated with alkalies at ordinary temperatures no decomposition takes place,

but when it is boiled with a strong solution of sodium hydroxide, ammonia is eliminated and the cyanogen group is converted into the carboxyl group. From the alkaline solution, after the reaction is over, acids precipitate the new substance, parasulphanilidobenzoic acid, as a white flocculent mass insoluble in water.

The acid is difficultly soluble in cold alcohol and ether, readily soluble in boiling alcohol. From the alcoholic solution it separates in feathery plates or needles, white and lustrous, somewhat resembling the crystals of parasulphaminebenzoic acid. It melts at 252–253° C., and at this temperature undergoes partial decomposition. The analytical results are as follows:

I. 0.2202 gram substance gave 0.1917 gram $BaSO_4$.

II. 0.2732 gram substance gave 0.2305 gram $BaSO_4$.

III. 0.3736 gram substance gave 16.95 cc. nitrogen at 23° C. and 762.1 mm.

IV. 0.3523 gram substance gave 16.20 cc. nitrogen at 23° C. and 761.3 mm.

	Calculated for $C_{13}H_{11}O_4SN$.	Found. I.	II.	III.	IV.
S	11.56	11.96	11.59	....	....
N	5.06	....	....	5.11	5.18

Barium Parasulphanilidobenzoate, $(C_{13}H_{10}NSO_4)_2Ba+5H_2O$. —This salt is beautifully crystallized, moderately soluble in boiling water, from which it crystallizes in concentric groups of very fine silky needles, very light and brittle. The salt melts with decomposition at a comparatively low temperature. The analyses are as follows:

I. 0.3897 gram salt lost 0.0446 gram H_2O, and gave 0.1149 gram $BaSO_4$.

II. 0.3026 gram salt lost 0.0350 gram H_2O, and gave 0.0889 gram $BaSO_4$.

	Calculated for $(C_{13}H_{10}NSO_4)_2Ba+5H_2O$.	Found. I.	II.
Ba	17.60	17.34	17.28
H_2O	11.54	11.44	11.56

Potassium Parasulphanilidobenzoate, $C_{13}H_{10}NSO_4K+2H_2O$. —This is very soluble in water, and crystallizes in short prisms. The analyses are as follows:

I. 0.2909 gram salt lost 0.0308 gram H_2O, and gave 0.0665 gram K_2SO_4.

II. 0.3565 gram salt lost 0.0360 gram H_2O, and gave 0.0819 gram K_2SO_4.

	Calculated for $C_{13}H_{10}NSO_4K+2H_2O$.	Found. I.	II.
K	11.11	10.26	10.31
H_2O	10.29	10.58	10.09

Paracyanbenzenesulphone toluide (p), $C_6H_4<^{CN}_{SO_2NHC_7H_7(p)}$. —The method of preparation of this compound, as well as of the compounds obtained by treating paracyanbenzenesulphone chloride with meta- and paratoluidins, is identical with that employed for the formation of the anilide. Two molecules of orthotoluidine are gradually added to one molecule of the chloride in chloroform or benzene solution.

The crude product is boiled with dilute hydrochloric acid and recrystallized from alcohol. The pure toluide crystallizes in well developed prismatic forms which sometimes occur as plates, and usually have a slight pink color. The melting-point of the orthotoluide is 122–123° C., and, like the anilide, it remains transparent until cooled much below its melting-point. The orthotoluide is slightly soluble in boiling water, under which it first melts, though not as readily as does the anilide. It dissolves in boiling alcohol and glacial acetic acid, but it is almost insoluble in ether. Treated with a solution of an alkali it dissolves unchanged, and it is reprecipitated by the addition of an acid, as a curdy white mass. Boiled with strong alkalies, ammonia is given off and the corresponding acid is formed. The analysis of the orthotoluide gave these results:

I. 0.2961 gram substance gave 0.2543 gram $BaSO_4$.

II. 0.2274 gram substance gave 0.1970 gram $BaSO_4$.

III. 0.3115 gram substance gave 28.30 cc. nitrogen at 17.1° C. and 761.3 mm.

IV. 0.2808 gram substance gave 23.72 cc. nitrogen at 17.4° C. and 758 mm.

	Calculated for $C_{14}H_{13}N_3O_4S$.	Found. I.	II.	III.	IV.
S	11.77	11.80	11.90	....	....
N	10.32	....	....	10.55	10.59

Parasulpho-o-toluidobenzoic acid, $C_6H_4<\begin{matrix}COOH\\SO_2NHC_7H_7(o)\end{matrix}$.—In general properties this acid closely resembles the anilido acid just described. It crystallizes from alcohol in light, flat needles of a pure white color, which melt at 246–247° C. and are decomposed at this temperature forming a dark-colored liquid. It is practically insoluble in boiling water or ether, but dissolves readily in boiling alcohol. The analytical results are as follows:

I. 0.2232 gram substance gave 0.1848 gram $BaSO_4$.

II. 0.2221 gram salt gave 0.1834 gram $BaSO_4$.

III. 0.3769 gram substance gave 16.10 cc. nitrogen at 20° C. and 760 mm.

IV. 0.3600 gram substance gave 17.80 cc. nitrogen at 21° C. and 760 mm.

	Calculated for $C_{14}H_{13}O_4SN$.	Found.			
		I.	II.	III.	IV.
S	11.01	11.37	11.35	....	....
N	4.82	....	....	4.87	4.98

To characterize the acid further, the barium salt was prepared. The crop of crystals separating from the solution on cooling was collected and the mother-liquor was then concentrated in order to obtain a further quantity of the salt. The portion of salt, however, which separated from the mother-liquor had a habit markedly different from the first fraction. Both were carefully recrystallized a number of times, but each retained its individuality. The analyses show that they differ in respect to the number of molecules of water of crystallization contained in them.

Barium Parasulpho-o-toluidobenzoate, $(C_{14}H_{12}O_4SN)_2Ba + 5H_2O$.—This salt crystallized first from the solution. It crystallized in minute white plates, moderately soluble in hot water. The results of the analyses are as follows:

I. 0.1956 gram salt lost 0.0220 gram H_2O, and gave 0.0562 gram $BaSO_4$.

II. 0.2090 gram salt lost 0.0240 gram H_2O, and gave 0.0606 gram $BaSO_4$.

	Calculated for $(C_{14}H_{13}O_4SN)_2Ba + 5H_2O$.	Found. I.	II.
Ba	16.99	16.89	17.05
H_2O	11.24	11.14	11.48

Barium Parasulpho-o-toluidebenzoate, $(C_{14}H_{13}O_4SN)_2Ba + H_2O$.—This salt was obtained from the mother-liquor of the salt above described. It is more soluble in water, and crystallizes in prismatic plates larger than the crystals of the first salt.

I. 0.2716 gram salt lost 0.0073 gram H_2O, and gave 0.0856 gram $BaSO_4$.

II. 0.4095 gram salt lost 0.0103 gram H_2O, and gave 0.1304 gram $BaSO_4$.

	Calculated for $(C_{14}H_{13}O_4SN)_2Ba + H_2O$.	Found. I.	II.
Ba	18.65	18.53	18.73
H_2O	2.45	2.68	2.52

This occurrence of two salts with different amounts of water of crystallization, noticed here, was noticed also in connection with the barium salts of the isomeric parasulpho-*m*-toluidobenzoic acid. The formation of analogous salts had been noticed also in the case of parasulphaminebenzoic acid. Remsen,[1] who was the first to prepare the acid and its salts, obtained a barium salt with 1 molecule of water of crystallization. Later, Noyes[2] prepared a salt with 5 molecules of water, and on further work showed that under different conditions both salts are formed. The principal causes of difference in composition were the degree of concentration and the rapidity with which the solution cooled.

Paracyanbenzenesulphonetoluide (*m*), $C_6H_4{<}^{CN}_{SO_2NHC_7H_7(m)}$.—From alcohol this compound separates in pure white prisms, melting at 128° C. It is less liable to change than the ortho- and paratoluides, and retains the pure white color, even on long standing. It closely resembles the orthotoluide in properties; is readily soluble in hot alcohol, and in glacial acetic acid; practically insoluble in boiling water and ether. Unlike the orthotoluide, it does not fuse under water. Alkalies dissolve it in the cold, and from the solution it is reprecipi-

[1] Am. Chem. (Liebig), 178, 302. [2] This JOURNAL, 7, 147.

tated by acids unchanged. Boiling with strong alkali produces the same kind of change as in the case of the orthotoluide, the corresponding acid being formed. The analyses gave the following figures:

I. 0.2493 gram substance gave 0.2184 gram $BaSO_4$.

II. 0.2166 gram substance gave 0.1890 gram $BaSO_4$.

III. 0.3652 gram substance gave 33.50 cc. nitrogen at 20.7° C. and 758.5 mm.

IV. 0.2853 gram substance gave 25.85 cc. nitrogen at 20° C. and 758.9 mm. pressure.

	Calculated for $C_{14}H_{13}O_3N_2S$.	Found. I.	II.	III.	IV.
S	11.77	12.03	11.98	....	....
N	10.32	....	....	10.42	10.33

Parasulpho-m-toluidobenzoic Acid, $C_6H_4<^{COOH}_{SO_2NHC_7H_7}$ (*m*). —The metatoluido acid is a beautifully crystallized compound which separates from the solution in alcohol in white, shining plates or leaflets, which have a tendency to assume the prismatic form. It melts with decomposition at 241–242° C. It is almost insoluble in boiling water and ether, but dissolves readily in boiling alcohol. The crystals of this acid are better defined than those of the orthotoluido acid, with a prismatic, rather than acicular habit. This, however, depends somewhat on conditions. The analyses gave the following results:

I. 0.2049 gram substance gave 0.1630 gram $BaSO_4$.

II. 0.2358 gram substance gave 0.1886 gram $BaSO_4$.

III. 0.3779 gram substance gave 16.45 cc. nitrogen at 24° C. and 765.5 mm.

IV. 0.2879 gram substance gave 12.80 cc. nitrogen at 23.6° C. and 770.3 mm.

	Calculated for $C_{14}H_{13}O_4SN$.	Found. I.	II.	III.	IV.
S	11.01	10.93	10.99	....	....
N	4.82	....	....	4.90	5.05

As in the case of the other acids described, the barium salt was prepared by boiling with an emulsion of barium carbonate and separating from the excess of carbonate by filtration. From this solution a salt crystallized out in long prisms, and,

upon further concentration of the mother-liquor, another crop of crystals was obtained which differed markedly from the first in form. Suspecting that these salts, as those of parasulpho-*o*-toluidobenzoic acid, differed in the amounts of water of crystallization, a separate analysis of each crop of crystals was made, which showed this to be the case.

Barium Parasulpho-m-toluidobenzoate $(C_{14}H_{12}O_4SN)_2Ba + 5H_2O$.—This salt separates first from the solution obtained by treating parasulpho-*m*-toluidobenzoic acid with barium carbonate. It is a little less soluble than the second modification, and crystallizes with 5 molecules of water in long transparent prisms. The analyses gave these results:

I. 0.2406 gram salt lost 0.0270 gram H_2O, and gave 0.0695 gram $BaSO_4$.

II. 0.2486 gram salt lost 0.0308 gram H_2O, and gave 0.0835 gram $BaSO_4$.

	Calculated for $(C_{14}H_{12}O_4SN)_2Ba + 5H_2O$.	Found. I.	II.
Ba	16.99	17.03	17.26
H_2O	11.14	11.24	10.83

Barium Parasulpho-m-toluidobenzoate, $(C_{14}H_{12}O_4SN)_2Ba + 3H_2O$.—This salt crystallizes from the mother-liquor of the first salt in glittering prismatic plates, resembling somewhat the crystals of potassium chlorate. It is slightly soluble in cold water, readily in hot. The analysis was as follows:

I. 0.4244 gram salt last 0.0307 gram H_2O, and gave 0.1270 gram $BaSO_4$.

	Calculated for $(C_{14}H_{12}O_4SN)_2 + 3H_2O$.	Found.
Ba	17.78	17.59
H_2O	7.00	7.23

Paracyanbenzenesulphonetoluide, $(p)C_6H_4<\begin{matrix}CN\\SO_2NHC_7H_7(p)\end{matrix}$. — Like the isomeric compounds this dissolves in hot alcohol and glacial acetic acid, but is practically insoluble in water, cold alcohol, or ether. From alcohol it crystallizes in rhombic prisms, usually tinged yellow, which melt at 151–152°. Alkalies dissolve it unchanged in the cold, but on heating the solution the corresponding acid, parasulpho-*p*-toluidobenzoic acid, is formed. The results of the analyses are as follows:

I. 0.2617 gram substance gave 0.2298 gram $BaSO_4$.

II. 0.2737 gram substance gave 0.2402 gram $BaSO_4$.

III. 0.2655 gram substance gave 23.90 cc. nitrogen at 22° C. and 756.7 mm.

IV. 0.2864 gram substance gave 26.10 cc. nitrogen at 20.5° C. and 766.1 mm.

	Calculated for $C_{14}H_{13}O_5N_2S$.	Found. I.	II.	III.	IV.
S	11.77	12.06	12.05	....	....
N	10.32	....	....	10.14	10.46

Parasulpho-p-toluidobenzoic acid, $C_6H_4<^{COOH}_{SO_2NHC_7H_7(p)}$.—Purified by recrystallization from alcohol, this compound is obtained in beautiful white plates or leaflets, sometimes with an acicular habit. It melts at 282–283° C. with decomposition, resembling in this respect the other members of the series. It is readily soluble in boiling alcohol, but almost insoluble in boiling water or ether. The analyses are as follows:

I. 0.2112 gram substance gave 0.1665 gram $BaSO_4$.

II. 0.3477 gram substance gave 0.2876 gram $BaSO_4$.

III. 0.3762 gram substance gave 17.00 cc. nitrogen at 20.8° C. and 761.2 mm.

IV. 0.3278 gram substance gave 14.75 cc. nitrogen at 21.4° C. and 762.5 mm.

	Calculated for $C_{14}H_{13}O_4SN$.	Found. I.	II.	III.	IV.
S	11.01	10.83	11.37	....	....
N	3.82	....	....	5.14	5.11

Barium Parasulpho-p-toluidobenzoate, $(C_{14}H_{12}O_4SN)_2Ba + H_2O$.—This salt crystallizes from water in small white prisms which show a tendency to curvature of the planes, and in some cases the crystals are considerably curled up at the ends. The crystals are not so well defined as are those of most of the other salts, and are more difficultly soluble in water. The analytical results are as follows:

I. 0.2827 gram salt lost 0.0041 gram H_2O, and gave 0.0879 gram $BaSO_4$.

II. 0.3345 gram salt lost 0.0089 gram H_2O, and gave 0.1045 gram $BaSO_4$.

	Calculated for $(C_{14}H_{10}O_4SN)_2Ba+H_2O$.	Found. I.	II.
Ba	18.65	18.30	18.38
H_2O	2.45	2.51	2.66

Formation of Parachlorcyanbenzene.—When a mixture of parasulphaminebenzoic acid and phosphorus pentachloride is heated in a retort as described under the preparation of paracyanbenzenesulphone chloride, reaction first takes place at comparatively low temperatures. By raising the temperature to 250° C. a further reaction takes place; sulphurdioxide is evolved, and parachlorcyanbenzene distils off as an oil which soon solidifies. The reaction is represented by this equation:

$$C_6H_4<\begin{matrix}COOH\\SO_2NH_2\end{matrix}+2PCl_5=C_6H_4<\begin{matrix}CN\\Cl\end{matrix}+2POCl_3+3HCl+SO_2.$$

It has been shown, however, that paracyanbenzenesulphone chloride is first formed, and that this then undergoes decomposition as represented by the equation:

$$C_6H_4<\begin{matrix}CN\\SO_2Cl\end{matrix}=C_6H_4<\begin{matrix}CN\\Cl\end{matrix}+SO_2.$$

The crude product obtained by distillation from the retort is placed in a flask and purified by distillation with steam, with which it is readily volatile.

Parachlorcyanbenzene, $C_6H_4<\begin{matrix}CN\\Cl(p)\end{matrix}$.—The compound closely resembles the isomeric ortho- and metachlorcyanbenzenes already studied by Henry,[1] and by Limpricht and Uslar,[2] respectively, in its general properties, having, however, a higher melting-point. It has a peculiar, rather pleasant aromatic odor, much resembling that of nitrobenzene, but more pungent. A marked property is its ready volatility. Sublimation takes place at low temperatures, and the compound is deposited in the form of long, glittering, prismatic needles, much like those obtained by careful sublimation of phthalic anhydride. Its melting-point is 93° to 94°. It dissolves slightly in boiling water, first melting to a clear oil, and, if the solution is kept at the boiling temperature, it passes off in

[1] Ber. d. chem. Ges., 2, 492. [2] Ann. Chem. (Liebig), 106, 35.

the steam. Alcohol and chloroform dissolve it readily. A curious property of the alcoholic solution was noticed. A hot solution was put aside to crystallize, and on cooling, parachlorcyanbenzene separated in long prismatic needles. On longer standing these needles were gradually dissolved, and a new crop of crystals, much shorter and thicker than the first lot, separated out. When boiled with alkalies, parachlorcyanbenzene is converted into parachlorbenzoic acid. The analyses gave these results:

I. 0.2300 gram substance gave 0.2394 gram AgCl.

II. 0.2413 gram substance gave 0.2488 gram AgCl.

III. 0.2338 gram substance gave 22.30 cc. nitrogen at 28° C. and 764.1 mm.

IV. 0.2371 gram substance gave 22.40 cc. nitrogen at 26° C. and 762 mm.

	Calculated for C_7H_4NCl.	Found. I.	II.	III.	IV.
Cl	25.78	25.74	25.50	....	....
N	10.21	....	....	10.50	10.49

For the purpose of comparison parachlorcyanbenzene was made from parachloraniline by diazotizing, and treating the resulting diazo compound with a solution of cuprous cyanide in potassium cyanide, according to the directions of Sandmeyer. The nitrile was separated by distilling the solution with steam, and it was found to be identical with the product obtained from parasulphaminebenzoic acid by treating it with phosphorus pentachloride.

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REVIEWS.

CHEMICAL TECHNOLOGY. BY GROVES AND THORP. VOL. II.—LIGHTING. BY W. Y. DENT, J. MCARTHUR, L. FIELD, F. A. FIELD, BOVERTON REDWOOD, AND D. A. LOUIS. Philadelphia: P. Blakiston, Son & Co. 1895. 8vo. 398 pp.

This book forms the second volume of the series of works on Chemical Technology, edited by Groves and Thorp. It deals with the methods of producing light, excepting gas and electric lighting only, which will form the subjects of a subsequent volume. The book is divided into six sections, each dealing with a class of related topics, which have more or less

direct bearing on the materials and means of producing light.

The first section, by W. Y. Dent, is a very good summary of the vegetable and animal fats and oils. The processes of saponifying fats are briefly explained, followed by an excellent synopsis of the usual methods employed in testing fats and oils; descriptions of the most important oils, their mode of extraction and purification with illustrations of the machinery used; characteristic reaction of each oil and the usual adulterants found in commercial samples.

Stearine is the subject of Section II, by John McArthur. In a short history of the industry, due credit is given to the researches of Chevreul on the fats, and to M. M. de Milby and Motard for establishing the industry on a practical basis. The raw materials and their valuation are reviewed briefly. Then follow descriptions of the various methods and apparatus for decomposing neutral fats into fatty acids, and the distillation, crystallization, and pressing of the fatty acids.

Candle manufacture is presented in Section III, by L. Field and F. A. Field. After a short review of the chronological development of the candle from the primitive torch, the authors discuss that important part of the candle,—the wick, and its preparation. Dipped and drawn candles are passed over quickly, and the greater part of the section devoted to moulded candles and the machines for making them. In all some fifteen different candle machines are described, and many of them illustrated by drawings.

Section IV, by Boverton Redwood, is devoted to the petroleum industry, forming the most important division of the book. The early history of petroleum is presented in an interesting manner, the different localities being discussed separately, with maps of many of the regions. The geology, origin, physical properties, and chemistry of petroleum, the methods of obtaining the crude oil in the several countries, and a short account of ozokerite mining in Galicia, follow. The description of oil-well drilling in the United States is largely compiled from the works of Peckham and Crew, and the catalogue of the Oil Well Supply Co., of Pittsburg, Pa., from which the illustrations of tools are taken. Petroleum refining comes next, considerable attention being given to the methods and apparatus used in the United States, but the refining of Russian, Canadian, and Galician oil is less completely described. A brief account of the transport of kerosene is followed by an extended description of the shale-oil industry, the various forms of apparatus being illustrated.

Lamps, other than gas and electric, form the topic of Section V, by Boverton Redwood. Beginning with the primitive

lamps of antiquity, the author traces the development of all varieties down to the present time. The subject is considered under two general heads,—lamps for fat oils and lamps for mineral oils. The various types of burners are illustrated and clearly explained. The reader is impressed by the great amount of mechanical ingenuity expended in attempts to secure the most perfect combustion of oil with highest illuminating efficiency. Drawings of nearly ninety varieties of lamps and burners are given. A discussion of accidents arising from the use of mineral oil lamps, and methods of preventing explosions, follows. Since the majority of accidents are caused by dropping or overturning lamps, rather than by explosion as such, the conclusion is reached that lamps should be constructed with metal reservoirs, so arranged that the flame cannot reach the interior and so ignite the mixture of air and oil vapor therein. Air and oil supply, chimneys, wicks, and extinguishing appliances, are fully treated. Mineral spirit, vapor and spray or blast lamps, air gas machines and carburettors and oil gas manufacture are included in this section.

Section VI is devoted to the consideration of miners' safety-lamps, by Boverton Redwood and D. A. Louis. This subject is treated under the following heads:—the development of safety lamps, their requisites, automatic extinction appliances, lamps intended to show the presence of fire-damp, modes of locking lamps, construction of the parts, and oils for use in safety lamps. This description of the numerous locking devices is a curious commentary on the recklessness of the miner in endangering his own and his comrades' lives by opening his lamp while at work.

The book is a valuable addition to the list of English handbooks on Technology. Although issued by an American publishing house, it is the work of Englishmen, and the American reader should bear in mind that the frequent allusions to practices "in this country," refer to England. The illustrations represent in most cases machinery and appliances manufactured by English or Continental firms. The typography is generally excellent and misprints are rare. On p. 45 occurs *cholrestin* for cholesterin, and on p. 207 we read "heavy hydrogen oils," where "hydrocarbons" would seem clearer. An excellent index adds to the worth of the volume.

FRANK H. THORP.

Correction: Vol. XVIII, p. 63, line 9 from bottom: Instead of the sentence beginning "It is peculiar" and ending "their specific gravity" insert the following: "It is worthy of note that the higher specific gravity observed in the crude Petrolia oil appears in all the fractions made *in vacuo*."